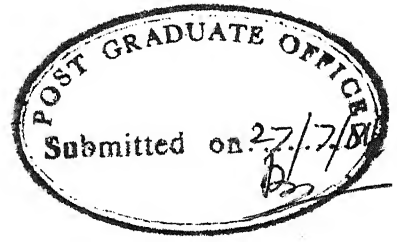


STUDIES ON SEGREGATION ROASTING OF OXIDISED COPPER AND NICKEL ORES

A thesis submitted
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by
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to the
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JULY, 1984



CERTIFICATE

This is to certify that the thesis entitled, 'STUDIES ON SEGREGATION ROASTING OF OXIDISED COPPER AND NICKEL ORES' by Shri K.R. Udayakumar has been carried out under my supervision, and this has not been submitted elsewhere for a degree.

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ABSTRACT

Segregation Roasting process for oxidised Copper and Nickel Ores has been investigated. Both the theoretical and experimental aspects have been examined. The thermodynamic analysis of the Segregation system involves the solution of a system of simultaneous nonlinear algebraic equations. In the present study, two numerical techniques namely Brown's method and Powell's hybrid method that overcome the deficiencies in the classical methods of solution of these equations have been employed. It is observed that both the methods lead to fast ultimate convergence, although Powell's method can accommodate a larger span of initial estimates of the unknowns. Solution of the equations has been used to assess the feasibility of the process in the case of Cu and Ni Segregation, and to predict the effect of the process parameters like temperature, amounts of chloride, reductant and moisture. The analysis indicates that qualitatively, Segregation is favourable in the case of Copper while some serious constraints hinder Nickel Segregation. Coupled with this, a generalised computational procedure that utilises the principle of minimisation of Gibbs' free energy has been attempted. It provided the equilibrium composition of both the gaseous and condensed species.

Laboratory scale experiments on Segregation Roasting has been carried out to atleast qualitatively predict the operating conditions required for Segregation of synthetic Oxidised Copper Ore.

LIST OF SYMBOLS

Chapter - 4

f_i	ith function
$f_{1x_j;h}$	1st difference quotient approximation
g_i	ith modified function of the original ith function
h^n	small positive number for finding the derivative
L_j	jth linear expression
N	number of unknowing
\underline{X}	set $(X_1, X_2, X_3, X_4, \dots, X_N)$
\underline{X}^n	approximation to the solution X^*
\underline{X}^*	solution of the system of equations

Chapter - 5

f_i	ith function in the system of equations
F	sum of the squares of the residuals
g	gradient of the function $F(x)$
J_{ij}	derivative of function f_i with respect to the variable x_j
M, E	determines the conditions for finishing the iterative process
$\alpha, \beta, ,$	scalars
	Displacement calculated by Newton iteration
\bar{J}	displacement actually added to the variable x_j
	step length specified before the start of the iterative process
\emptyset	predicted value of the sum of the squares

Chapter -- 6

a	elemental composition matrix
b	elemental total in mixture, moles
f	free energy function of individual species, J/mol
F^*	Gibbs free energy, J/mole
F	free energy function
i,j,k, l,e	integers
m	number of gaseous species in mixture
NE	number of elements
\emptyset	total pressure atmospheres
R	gas constant 1.987 J/mole- $^{\circ}$ K
T	temperature $^{\circ}$ K
X	number of moles
y	value of X at previous iteration
\bar{X}	sum of the number of moles of gaseous species
\bar{y}	sum of the values of X at previous iteration
L	Lagrangian function
	difference between X and y

Superscripts

g	denotes gaseous species
s	denotes condensed species

CHAPTER 1

INTRODUCTION

Oxidised Copper Ores are commonly concentrated either by Flotation or by Leaching. However, flotation is not possible when the copper minerals are locked with the gangue or when the copper minerals are mainly silicates, and leaching is uneconomic when the presence of limestone or dolomite in the gangue causes excessive acid consumption.

The segregation roasting process (which now onwards would be referred to as segregation process) provides an alternate method for treating oxidised copper ores by extracting the copper from the ore minerals at red heat and reprecipitating it as a metal on finely divided carbon which is admixed with the Ore. After cooling, in the absence of air, or quenching, the copper is recovered in a high grade concentrate by flotation.

In practice, the process involves the addition of 1-1.5% fine coal or coke and 0.3 to 1 percent sodium chloride to the ground Ore, and heating to temperature of the order of 800°C. The basic steps considered to occur are :

1. The salt is hydrolysed by moisture in the presence of silica, Aluminosilicates and other clay minerals to form hydrogen chloride.

2. The Hydrogen chloride reacts with the Copper Oxide in the Ore producing H_2O and a volatile chloride, generally agreed to be predominantly the copper (I) chloride trimer.
3. The Cuprous chloride is reduced by Hydrogen in the vicinity of the carbon particles to form the segregated metallic copper, at the same time regenerating Hydrogen chloride.

Under optimum conditions mild reducing conditions prevail in the segregation chamber, and thus the copper concentrates in the stronger reducing environment of the carbonaceous reagents.

The process continues in a cyclic manner and amounts of chloride and Hydrogen considerably less than the stoichiometric are required. The segregation process also recovers Gold or Silver that may be in the Copper Ore - metals that are usually lost in the tailings during Acid or Ammonia Leaching. Ores of many metals that form volatile chlorides or Oxy-chlorides may respond to the segregation process. It has been suggested that Antimony, Bismuth, Cobalt, Gold, Lead, Nickel, Palladium, Silver and Tin may be treated in this manner. In recent years, the process has been extended to Roasted concentrates and selective segregation of Copper from Copper-Nickel concentrates.

Scope of Present Work :

In our country, there are deposits of oxidized copper and Nickel Ores which have hitherto not been exploited fully due to

the lack of a viable process for extraction, and in this background, the segregation process seems to be a potential one that necessitates a deeper theoretical and experimental study. As elucidated earlier, segregation process is typical of those systems involving many or complex equilibria, a thermodynamic evaluation of which involves the numerical solution of a system of simultaneous nonlinear equations. These are generally solved by :

- 1) Trial and Error approach or graphical method
- 2) Classical methods of solution of nonlinear equations.

The first approach becomes extremely tedious and time consuming when many sets of numerical values of the thermodynamic variables are required; the second approach not very infrequently runs aground when the variables vary over a wide range, or when the flat start values are far away from the actual zeros of the equations.

In the present study, Algorithms that overcome these deficiencies are applied to assess the thermodynamic feasibility of the segregation process for the extraction of Cu and Ni from low grade Oxide Ores. Further, the effect of a number of process variables on segregation is predicted. Although the numerical technique is exemplified for the segregation process, it would be applicable for any heterogeneous system. Further, a generalised computational scheme that includes both the gaseous and condensed

species has been employed in the determination of equilibrium compositions by minimising the Gibb's Free energy. Secondly, laboratory batch tests on synthetic Copper Ore for the extraction of Copper by the segregation process were designed to study the effect of process variables.

CHAPTER 2

LITERATURE REVIEW

The subject of Segregation Process has spawned an enormous literature under various headings : Segregation chemistry⁽⁵⁻¹¹⁾, Thermodynamic⁽¹⁻⁴⁾ and Kinetic aspects⁽²⁵⁻²⁶⁾, Pilot and Commercial Operations⁽¹²⁻²⁴⁾, Effect of various Reagents on Segregation etc., an exhaustive review of which is given by Habashi⁽⁶⁾. In this review, only the Thermodynamic aspects of Segregation Process are considered.

Hitherto, a detailed study from the Thermodynamic standpoint has been made by Iwasaki⁽¹⁾ and Yazawa⁽²⁾, the former by employing Oxygen-chlorine potential diagram, and the latter by combining stoichiometric relations with equilibrium constants.

Iwasaki⁽¹⁾ constructed Equilibrium diagrams showing the stability regions of oxides and chlorides of metals, and superimposing them for comparison.

An equilibrium diagram for Cu-H₂-HCl and Fe-H₂-HCl at 750°C and at constant partial pressures of water vapor of 0.3 atm and 0.03 atm were constructed. It is found that the effect of water vapor concentration on the relative positions of the equilibrium lines is small for both copper and iron. There is

a marked difference in the stability fields of the 2 systems indicating that the Copper Oxides may be readily converted to CuCl , whereas the Iron Oxides remain as Oxides. The figure also indicates :

1. that too strong a reducing atmosphere may reduce the copper oxides to metallic copper in place, and the resultant metallic copper may not be chlorinated (reduction in situ)
2. that a moderately reducing atmosphere helps the chloridisation of Cupric Oxide
3. an excessive amount of Oxygen in the atmosphere would interfere with the process by preventing the conversion of both CuO and CuCl and also of CuCl to metallic Cu .

A similar diagram involving the systems $\text{Ni-H}_2\text{-HCl}$ and $\text{Fe-H}_2\text{-HCl}$ at 950°C and at the water vapor concentrations of 3% and 30% by volume were constructed. The stability fields of Nickel and Iron chlorides overlap very closely and the partial pressure of HCl required to chloridize Nickel is a few orders of magnitude greater than that for Copper which is in good agreement with a laboratory observation that a relatively large quantity of Salt is required to effect Nickel Segregation and that CaCl_2 is more effective than NaCl .

A metal chloride formed must be volatilised and transported to a precipitation site, most commonly at the surface of a solid reductant where it is reduced. Brewer and Lofgren⁽⁴⁾ established that cuprous chloride exists as the trimer $\text{Cu}_3\text{Cl}_3(\text{g})$ which dissociates into the monomer $\text{CuCl}(\text{g})$ at high temperatures, that cuprous chloride is almost entirely in the form of the trimer in the neighbourhood of 800°C , and that no evidence was found for the presence of the dimer.

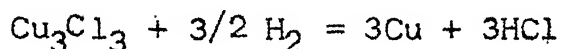
Kubaschewski and Evans⁽²⁷⁾ plotted the vapor pressures of the chlorides of several metals of interest in segregation roasting against temperature. A high equilibrium vapor pressure may be indicative of a successful transport of a metal chloride. According to Rey^(19,20) Ferrous chloride has a high enough vapor pressure, but Iron cannot be segregated along with Copper since water vapor decomposes Iron chlorides to form Magnetite. The vapor pressure of AgCl in the relevant temperature range being very low (10^{-2} mm Hg), Segregation of Ag is unsuccessful. Apparently, Copper functions as a carrier of Gold and Silver.

It is observed that each element has the relatively well defined regions of stability of its Oxides and chlorides and the relative positions of these regions change very little with temperature or water vapor concentration. This lead Iwasaki⁽¹⁾ to construct equilibrium diagrams at 750°C of several metals of

interest in Segregation Roasting. From these diagrams, it may be speculated that Pb may respond to Segregation; Iron and Manganese may not respond to Segregation as their Oxides are the stable species (at this temperature).

According to Rey^(19,20), segregation atmosphere cleans the gold surface and improves its flotability. Cobalt appears to be more easily chloridised than Nickel, but the partial pressure of hydrogen required to reduce it is higher than that required by Nickel.

The accepted mechanism on the precipitation of metallic copper on carbon particles is the reduction of cuprous chloride vapor by H_2 in the vicinity of carbon particles⁽²⁵⁾



Inability of carbon as a reducing agent for metal chloride may be inferred from the thermodynamic consideration of the reaction (Kellog⁽³⁾)



Rey⁽²⁰⁾, however, showed that in the presence of a small amount of water vapor, its reaction with carbon produces hydrogen, and the reduction of metal chlorides becomes possible. The presence of a solid reductant that provides nuclei for precipitation and growth of metallic copper from cuprous chloride vapor, and that releases H_2 at a controlled rate, appears essential for the

process. Thus less active the carbonaceous material, the more difficult it will be for Copper to precipitate.

A thermodynamic Evaluation of Segregation process was performed by Yazawa⁽²⁾ by assuming establishment of local equilibria in each step at each site. This was done by juxtaposing the thermodynamic relations arising out of the Mass action equations with the stoichiometric relationships for which, feed pellets of Copper and Nickel Oxides with the typical compositions were segregation roasted in a Lab scale Experiment. The solution of the resulting set of nonlinear equations were presented in a plot of the partial pressures of the various gaseous species against Oxygen potential. From the resulting profiles, of Copper and Nickel Segregation systems, Yazawa concluded that the fundamental reaction calculations are promising for Copper whereas serious restrictions hinder Nickel Segregation.

CHAPTER 3

STRUCTURE OF THE PROBLEM

The Segregation Process involves a complex set of reactions, occurring at adjacent sites in a mixture consisting of the Ore, Salt and Carbon. For a thermodynamic analysis, chemical equilibrium is assumed in the system, and the equilibrium constant method is employed.

In a typical Cu Segregation system, the predominant gaseous species at equilibrium are CO , CO_2 , H_2 , H_2O , CuCl , Cu_3Cl_3 , HCl and FeCl_2 . For the 3 nonmetals C, H, Cl, expressions for the conservation of masses may be written, ' n_i ' indicating the number of moles of the chemical species i . These expressions are :

$$\text{C balance} : n_{\text{C}} = n_{\text{CO}} + n_{\text{CO}_2} \quad (3.1)$$

$$\text{H}_2 \text{ balance} : n_{\text{H}_2} = n_{\text{H}_2} + n_{\text{H}_2\text{O}} + 1/2 n_{\text{HCl}} \quad (3.2)$$

$$\text{Cl balance} : n_{\text{Cl}} = n_{\text{HCl}} + 2n_{\text{FeCl}_2} + 3n_{\text{Cu}_3\text{Cl}_3} + n_{\text{CuCl}} \quad (3.3)$$

The partial pressures of the gaseous species i are defined by

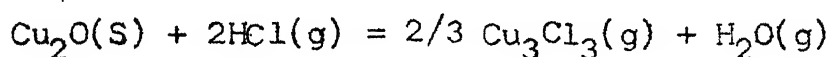
$$p_i = \frac{n_i}{n_T} P$$

n_T being the total number of moles, and P , the total pressure.

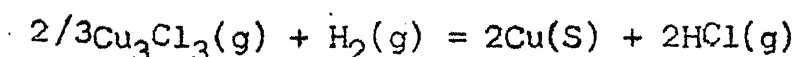
Here,

$$n_T = n_{CO} + n_{CO_2} + n_{H_2} + n_{H_2O} + n_{HCl} + n_{CuCl} + n_{Cu_3Cl_3} + n_{FeCl_2} \quad (3.4)$$

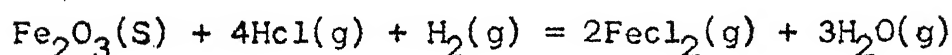
Equations (3.5) to (3.11) constitute the equilibrium identified in the Copper Segregation system along with the expressions for the equilibrium constant at a particular temperature.



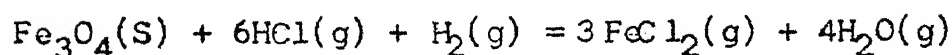
$$K_5 = n_{Cu_3Cl_3}^{2/3} \cdot n_{H_2O} \cdot n_T^{1/3} / n_{HCl}^2 \quad (3.5)$$



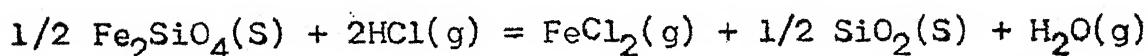
$$K_6 = n_{HCl}^2 / n_{Cu_3Cl_3}^{2/3} \cdot n_{H_2} \cdot n_T^{1/3} \quad (3.6)$$



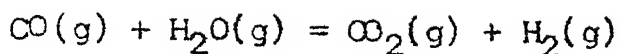
$$K_7 = n_{FeCl_2}^2 \cdot n_{H_2O}^3 / n_{HCl}^4 \cdot n_{H_2} \quad (3.7)$$



$$K_8 = n_{FeCl_2}^3 \cdot n_{H_2O}^4 / n_{HCl}^6 \cdot n_{H_2} \quad (3.8)$$



$$K_9 = n_{FeCl_2} \cdot n_{H_2O} / n_{HCl}^2 \quad (3.9)$$



$$K_{10} = n_{\text{CO}_2} \cdot n_{\text{H}_2} / n_{\text{CO}} \cdot n_{\text{H}_2\text{O}} \quad (3.10)$$



$$K_{11} = n_{\text{Cu}_3\text{Cl}_3} \cdot n_{\text{T}}^2 / n_{\text{CuCl}}^3 \quad (3.11)$$

If the value of n_{C} , n_{H_2} , n_{Cl} are known (from experiments), the following equations may be solved simultaneously, at a given CO_2/CO ratio :

Eq. (3.1), (3.2), (3.3) and (3.4)

Eq. (3.5) or (3.6)

Eq. (3.7) or (3.8) or (3.9)

Eq. (3.10) or (3.11)

The equilibrium ($p_{\text{CO}_2}/p_{\text{CO}}$) ratios at which the solid species Fe_2O_3 , Fe_3O_4 , Fe_2SiO_4 , Cu and CuO are stable is delineated in Appendix 3.2.

The solution of the system of simultaneous Nonlinear Algebraic equations outlined above yield the localised concentrations of the various gaseous species.

In a subsequent chapter, the feasibility of the process is assessed from the plot of the partial pressures of the gases generated against the Oxygen potential.

The stoichiometric values may be varied from the base value, and comparison of the resulting partial pressures of the various gaseous species with the base value aids in the prediction of the effect of the process variables in the segregation system.

Nickel Segregation System

Analogous treatment as in the case of Copper may be extended to Nickel for a thermodynamic evaluation. In the Nickel Segregation system, the predominant gaseous species constitute CO, CO₂, H₂, H₂O, HCl, NiCl₂ and FeCl₂.

The stoichiometric relations are :

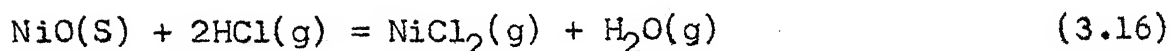
$$\text{C balance} \quad : \quad n_{\text{C}} = n_{\text{CO}} + n_{\text{CO}_2} \quad (3.12)$$

$$\text{H}_2 \text{ balance} \quad : \quad n_{\text{H}_2} = n_{\text{H}_2} + n_{\text{H}_2\text{O}} + 1/2 n_{\text{HCl}} \quad (3.13)$$

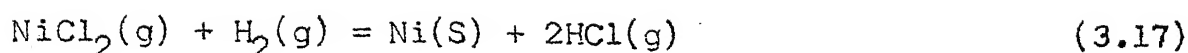
$$\text{Cl}_2 \text{ balance} \quad : \quad n_{\text{Cl}_2} = 1/2 n_{\text{HCl}} + n_{\text{FeCl}_2} + n_{\text{NiCl}_2} \quad (3.14)$$

$$\begin{aligned} n_{\text{T}} &= n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{H}_2} + n_{\text{H}_2\text{O}} + \\ &\quad n_{\text{HCl}} + n_{\text{NiCl}_2} + n_{\text{FeCl}_2} \end{aligned} \quad (3.15)$$

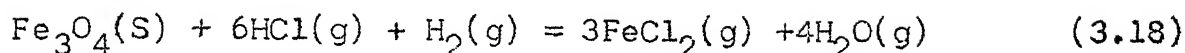
The thermodynamic relations are :



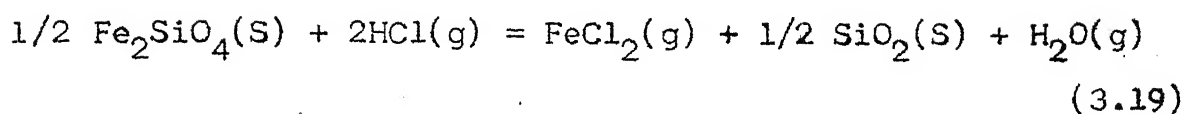
$$K_5 = n_{\text{NiCl}_2} \cdot n_{\text{H}_2\text{O}} / n_{\text{HCl}}^2$$



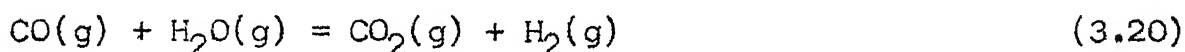
$$K_6 = n_{\text{HCl}}^2 / n_{\text{NiCl}_2} \cdot n_{\text{H}_2}$$



$$K_7 = n_{\text{FeCl}_2}^3 \cdot n_{\text{H}_2\text{O}}^4 / n_{\text{HCl}}^6 \cdot n_{\text{H}_2}$$



$$K_8 = n_{\text{FeCl}_2} \cdot n_{\text{H}_2\text{O}} / n_{\text{HCl}}^2$$



$$K_9 = n_{\text{CO}_2} \cdot n_{\text{H}_2} / n_{\text{CO}} \cdot n_{\text{H}_2\text{O}}$$

As in the case of copper, outlined in the previous section, the unknowns CO , CO_2 , H_2 , H_2O , FeCl_2 , HCl and NiCl_2 may be obtained solving the following system of Nonlinear equations (simultaneously) :

Eqs. (3.12) to (3.15)

Eqns. (3.16) or (3.17)

Eqs. (3.18) or (3.19)

Eq. (3.20)

The equilibrium $(p_{\text{CO}_2}/p_{\text{CO}})$ ratios at which the solid species NiO , Ni , Fe_3O_4 and Fe_2SiO_4 are stable is given in Appendix 3.2.

The Equilibrium constants were obtained from the Free energy data, at the temperature of interest.

Analysis similar to the one delineated in the case of Copper Segregation, including the variation of the process variables, is employed in the Nickel system too.

The next chapter outlines the Algorithms employed for solving the equations, followed by discussions on the results so obtained.

CHAPTER 4

METHODS OF SOLUTION

As stated in the Introduction, this chapter discusses 2 Algorithms that generally overcome the deficiencies implicit in the solution of a system of simultaneous Nonlinear Algebraic equations by the classical methods.

In the preceding chapter, the problem had been formulated as the solution of solving N real equations in N real unknowns; the system being given as

$$\begin{aligned} f_1(\underline{X}) &= f_1(X_1, X_2, X_3, \dots, X_N) = 0 \\ f_2(\underline{X}) &= f_2(X_1, X_2, X_3, \dots, X_N) = 0 \\ &\vdots \\ f_N(\underline{X}) &= f_N(X_1, X_2, X_3, \dots, X_N) = 0 \end{aligned} \quad (4.1)$$

BROWN's Method :

This is a local method^(36,37,40) which handles the function (4.1) one at a time so that ^{the} information obtained from working with f_1 can be incorporated when working with f_2 etc. A successive substitution scheme is used rather than the simultaneous treatment of the f_i characteristic of Newton's method. Brown's method is derivative free; moreover, second order convergence has been proven.

Step 1 :

Let \underline{X}^n denote an approximation to the solution \underline{X}^* of (4.1). Expand the first function f_1 in an approximate Taylor series expansion about the point \underline{X}^n .

$$f_1(\underline{X}) \sim f_1(\underline{X}^n) + f_{1X_1;h}(\underline{X}^n) (X_1 - X_1^n) + f_{1X_2;h}(\underline{X}^n) (X_2 - X_2^n) + \dots \\ \dots f_{1X_N;h}(\underline{X}^n) (X_N - X_N^n) \quad (4.2)$$

where $f_{1X_j;h}(\underline{X}^n)$ is defined to be the first difference quotient approximation.

If \underline{X}^n is chosen close enough to \underline{X}^* , $f_1(\underline{X}) \sim 0$, and solving for that variable, say X_N , whose corresponding approximate partial derivative $f_{1X_N;h}(\underline{X}^n)$, is largest in absolute value, we have

$$X_N = X_N^n - \sum_{j=1}^{N-1} (f_{1X_j;h}^n / f_{1X_N;h}^n) (X_j - X_j^n) - f_1^n / f_{1X_N;h}^n \quad (4.3)$$

where $f_{1X_j;h}^n \equiv f_{1X_j;h}(\underline{X}^n)$

and $f_1^n \equiv f_1(\underline{X}^n)$

From (4.3), it may be noted that X_N is a linear function of the $N-1$ variables, and may be renamed $L_N(X_1, X_2, X_3, X_4, \dots, X_{N-1})$.

Step 2 :

A new function g_2 of the $N-1$ variables $X_1, X_2, X_3, \dots, X_{N-1}$ may be defined, which is related to the second function f_2 , as

$$g_2(x_1, x_2, x_3, \dots, x_{N-1}) \equiv f_2(x_1, x_2, \dots, x_{N-1}, L_N(x_1, x_2, \dots, x_{N-1}))$$

Let g_2^n be defined as $g_2^n = f_2(x_1^n, x_2^n, \dots, x_{N-1}^n, L_N^n)$

Now expand g_2 in an approximate Taylor series expansion about the point $(x_1^n, x_2^n, \dots, x_{N-1}^n)$, linearise (ignoring higher order terms) and solve for that variable, say x_{N-1}^n , whose corresponding partial derivative $g_{2x_{N-1};h}$, is largest in magnitude :

$$x_{N-1} \equiv x_{N-1}^n - \sum_{j=1}^{N-2} (g_{2x_j;h}^n / g_{2x_{N-1};h}^n) \cdot (x_j - x_j^n) - g_2^n / g_{2x_{N-1};h}^n$$

where

$$g_{2x_j;h}^n \equiv \frac{g_2(x_1^n, x_2^n, \dots, x_{j-1}^n, x_j^n + h^n, x_{j+1}^n, \dots, x_{N-1}^n) - g_2^n}{h^n}$$

where h^n is a small positive number.

$$\text{Again, } x_{N-1} = L_{N-1}(x_1, x_2 \dots x_{N-2})$$

Step 3 :

$$g_3(x_1, x_2, \dots, x_{N-2}) = f_3(x_1, x_2, \dots, x_{N-2}, N-1, N)$$

The basic processes of Taylor expansion, linearisation, equating to zero and solving for one variable, say x_{N-2} , (whose corresponding approximate partial derivative $g_{3x_{N-2};h}$ is largest in magnitude) is followed.

The procedure is continued in this fashion, eliminating one variable for each equation treated. Every time a new linear expression L_{N-k} is obtained, for one of the variables, say x_{N-k} , in terms of the remaining $N-k-1$ variables, $x_1, x_2, x_3, \dots, x_{N-k-2}, x_{N-k-1}$ this linear expression is used wherever x_{N-k} had appeared in the previously defined expressions $L_{N-k+1}, L_{N-k+2}, \dots, L_{N-1}, L_N$.

Step N : At this stage, we have

$g_N = f_N(x_1, L_2, L_3, L_4, \dots, L_N)$ where the L_j 's are obtained by back substitution in the $N-1$ rowed triangular linear system which now has the form

$$L_i = x_i^n - \sum_{j=1}^{i-1} (g_{N-i+1, x_j}^n / g_{N-i+1, x_i}^n) \cdot (L_j - x_j^n) \\ - g_{N-i+1}^n / g_{N-i+1, x_i}^n, \quad i = N, N-1, \dots, 2$$

(with $g_1 \equiv f_1$ and $L_1 \equiv x_1$) so that g_N is just a function of the single variable x_1 . Now expanding, linearising and solving for x_1 , we obtain

$$x_1 = x_1^n - g_N^n / g_{N, x_1}^n.$$

The point x_1 thus obtained is used as the next approximation x_1^{n+1} , to the first component x_1^* , of the solution vector \underline{x}^* . x_1 is renamed as L_1 and the L_j system is backsolved to get improved approximation to the other components of \underline{x}^* .

Brown's technique is a fast local technique, that leads to convergence if the start values are in a region of local convergence. To check the results obtained from the Brown's method, as also to assess the viability of the method for a general simultaneous Nonlinear Equation problem, the Hybrid method of Powell that places no restriction on the initial estimate of the unknowns being 'sufficiently close' to the solution of the equations, was used. A general description of the method follows.

POWELL's Hybrid Method⁽³⁸⁾ :

Most Algorithms for the solution of systems of simultaneous Nonlinear equations are centred around either of the 2 approaches :

1. Model expanded as Taylor series and corrections to several parameters calculated at each iteration on the assumption of local linearity.
2. Various modifications of steepest descent methods used.

Both these methods not infrequently fail, Taylor's series method due to divergence of successive iterates, and the steepest descent methods because of very slow convergence after the first few iterations. Powell's method combines both the Newton and steepest descent methods in such a way as to give steady progress and a fast rate of ultimate convergence.

To begin the Kth iteration, the estimate of the solution x^k , a step length $\Delta^{(k)}$ and 2 numbers E and M are required. The step can be changed on each iteration, and its purpose is to restrict the length of the displacement $(x^{(K+1)} - x^{(K)})$ in order that the iteration decreases the value of $F(x)$ where $F(x)$ is the sum of the square of the Residuals

$$F(x) = \sum_{i=1}^N (f_i(x))^2$$

E and M determine the conditions for finishing the iterative process. It finishes if the value of $F(x)$ is reduced to less than E, or alternatively if the gradient of $F(x)$ is so small that the distance from x to a solution is predicted to exceed M.

First, the kth iteration calculates the elements of the Jacobian Matrix

$$J_{ij}^{(k)} = \left. \frac{\partial f_i}{\partial x_j} \right|_{x=x^{(k)}} \quad (4.5)$$

and then it evaluates the full Newton-Raphson correction $\delta^{(k)}$ by solving the linear system

$$f_i(x^k) + \sum J_{ij}^{(k)} \delta_j^{(k)} = 0 \quad (4.6)$$

and also the gradient $g^{(k)}$ of $F(x)$ at $x^{(k)}$ by calculating the components

$$g_j^{(k)} = \left[\frac{\partial}{\partial x_j} F(x) \right]_{x=x^{(k)}} \quad (4.7)$$

It then tries the test

$$F(x^{(k)}) \geq M ||g^{(k)}||_2 \quad (4.8)$$

and if it holds, the iterative process ends because of the likelihood that the sequence of estimates $x^{(k)}$ is converging not to a solution of the equations but to a local minimum of $F(x)$.

If the condition (4.8) does not hold, then a displacement $\bar{s}^{(k)}$ is calculated to add to the vector $x^{(k)}$. This displacement is just the classical correction $s^{(k)}$ if $\Delta^k \geq ||s^{(k)}||_2$.

But if

$$\Delta^{(k)} < ||s^{(k)}||_2 \quad (4.8.1)$$

then $\bar{s}^{(k)}$ is made equal to $\Delta^{(k)}$.

In this case the displacement has the form

$$\bar{s}^{(k)} = \alpha_1 s^{(k)} + \beta_1 g^{(k)} \quad (4.9)$$

where α_1 and β_1 are scalars.

$\alpha_1 = 0$ if the step along the steepest descent vector of $F(x)$

$$\bar{s}^{(k)} = -\Delta^{(k)} g^{(k)} / ||g^{(k)}||_2 \quad (4.10)$$

does not go beyond the predicted minimum of $F(x)$ along the steepest descent vector from $x^{(k)}$, this predicted minimum being at the point

$$x^{(k)} - \left[\frac{1}{2} \|g^{(k)}\|_2^2 / \|J^{(k)} g^{(k)}\|_2^2 \right] g^{(k)} \quad (4.11)$$

So the condition

$$\Delta^{(k)} \leq \frac{1}{2} \|g^{(k)}\|_2^3 / \|J^{(k)} g^{(k)}\|_2^2 \quad (4.12)$$

is tried and if both the inequalities (4.8.1) and (4.12) hold then $\bar{\delta}^{(k)}$ is defined by (4.10). In the case when condition (4.8.1) is satisfied, but (4.12) is not satisfied, the point $(x^{(k)} + \bar{\delta}^{(k)})$ is let to be on the straight line joining the point (4.11) to the point $(x^{(k)} + \delta^{(k)})$.

Thus $\bar{\delta}^{(k)}$ interpolates between the steepest descent and the classical Newton Raphson correction. The functions $f_i(x)$ are calculated at the incremented value $(x^{(k)} + \bar{\delta}^{(k)})$. If

$$F(x^{(k)} + \bar{\delta}^{(k)}) < F(x^{(k)}) \quad (4.13)$$

$$\text{is satisfied, then } x^{(k+1)} = x^{(k)} + \bar{\delta}^{(k)} \dots \quad (4.14)$$

and the convergence criterion is tested. However, if (4.13) fails,

$x^{(k+1)} = x^{(k)}$, and test (4.15) leads to a reduction in the step length $\Delta^{(k)}$.

Revision of the step length $\Delta^{(k)}$ constitutes the last stage of the iteration which depends on the predicted value of the sum of squares of Residuals at $(x^{(k)} + \bar{\delta}^{(k)})$

$$\phi^{(k)} = \sum [f_i(x^{(k)} + \sum J_{i,j}^{(k)} \delta_j^{(k)})]^2 \quad (4.15)$$

which is less than $F(x^{(k)})$. If the predicted value is found so bad that the actual value of the sum of squares satisfies the inequality

$$F(x^{(k)} + \bar{s}^{(k)}) > (1-\epsilon) F(x^k) + \epsilon \phi^k \quad (4.16)$$

where ϵ is a constant from $(0,1)$, then it is concluded that the linear approximations to the functions $f_i(x)$ desired from the Jacobian elements (4.5) are not adequate over the distance $\|s^{(k)}\|_2$. Therefore, $\Delta^{(k)}$ is reduced by multiplying it by a factor λ , $0 < \lambda < 1$.

CHAPTER 5

RESULTS AND DISCUSSION

In the application of the Algorithms to the Segregation problem, the structure of the problem was modified by converting the thermodynamic variables (namely the mole numbers) into their logarithmic values. This was done to prevent one of the variables from assuming a negative value (since negative mole numbers have no physical significance) and secondly, with a view to let the variables to be of similar magnitude in the region of interest, and avoid cancellation errors in the evaluation of the objective function.

In the modified form, both Brown's local method and Powell's Hybrid method showed enormous rigidity. Since the bane of all methods of solution of Nonlinear equations is the initial guess values, these were varied over a wide range of values. Flat start values with as remote a value as 10^{-7} upto 10^{+7} through zero yielded convergence in the case of Powell's method, while Brown's method diverged for very low values of 10^{-2} through 10^{-7} , converging for values from 0 to 10^{+7} . Thus, between the two, Powell's method showed greater stability. This arises from the fact that Powell's Algorithm shares with the gradient methods their ability to converge from an initial guess value which may be outside the region of convergence of other methods. The Algorithm shares with the Taylor series

method the ability to close in on the converged values rapidly after the vicinity of the converged values has been reached, thus combining the best features of its predecessors while avoiding their serious limitations.

Copper Segregation :

For the thermodynamic analysis of Cu Segregation that require the stoichiometric values desired from experiment, the typical values of Yazawa have been made use of. This is a 100g pellet of Cu, consisting of 2% Cu, 20% Fe, 1% NaCl, 1% C (and rest as gangue). The value of K at ambient pressure, and at the temperature of interest is calculated from the free energy data⁽³⁰⁾. The resulting Nonlinear equations were solved by the methods outlined in the preceding chapter. The results of the computation at a Segregation temperature of 1100°K is tabulated in Table 5.1. (for various values of CO_2/CO ratio). The evolved gas consists predominantly of, CO_2 , H_2O , H_2 , while the profiles of the other gaseous species vary depending on the oxygen potential. In confirmity with the very high dissociation constant of the monomer - Trimer Chloride Equilibria, the partial pressure of the monomer is very low in the Cu Segregation system.

The plot (Fig. 5.1) of the partial pressures of the gaseous species against the oxygen potential indicates that the partial pressure of Cu_3Cl_3 is high in the region where Cu_2O exists, implying thereby that the chlorination reaction (3.5)

proceeds forward. It decreases as the oxygen potential decreases, while the partial pressure of HCl increases, showing the occurrence of eqn. (3.6), yielding copper. The HCl (g) thus produced would be recycled and utilised in the chlorination of Cu_2O , represented by eqn. (3.5). The gradients of the various gaseous species may therefore be directly related to the mechanism of the process. It may be noted that among the chlorides, Cu_3Cl_3 and HCl determine the direction of the process while FeCl_2 plays no major role.

The effect of the process variables, namely the amount of reductant, water, chloride and the temperature may be studied by varying the input compositions of the reactants, and substituting the appropriate values of the Equilibrium constants at different temperatures. The results of this exercise may be plotted as shown in Figs. 5.2 to 5.5. The variations of these parameters exhibit a definite trend in the profiles of the gaseous species, from which conclusions may be drawn from the thermodynamic standpoint. If an increase in partial pressure of Hydrogen chloride over the base value be maintained as the yard stick for enhanced Cu segregation, it may be seen that decreasing the temperature, decreasing the amount of water, increasing the amount of NaCl, and decreasing the amount of carbon aids segregation. A higher amount of carbon leads to insitu reduction of the oxide, suppressing chloridisation, and an excessive amount of water dilutes the effect of the chloride.

Table 5.1

Logarithmic equilibrium partial pressures of the gaseous species
at varied $\log (p_{\text{CO}_2}/p_{\text{CO}})$ values at 1100°K

	CO	CO ₂	H ₂	H ₂ O	HCl	CuCl	Cu ₂ Cl ₃	FeCl ₂
1	2	3	4	5	6	7	8	9
0.00	-0.385	-0.885	-0.515	-0.652	-0.833	-5.070	-4.672	-2.171
0.25	-1.028	-0.778	-0.653	-0.441	-0.825	-4.993	-4.445	-2.267
0.50	-1.203	-0.704	-0.825	-0.352	-0.821	-4.903	-4.175	-2.337
0.75	-1.405	-0.655	-1.023	-0.311	-0.819	-4.802	-3.870	-2.384
1.00	-1.626	-0.623	-1.241	-0.279	-0.818	-4.692	-3.542	-2.415
1.25	-1.858	-0.608	-1.472	-0.256	-0.820	-4.579	-3.202	-2.438
1.50	-2.097	-0.597	-1.710	-0.247	-0.825	-4.465	-2.860	-2.460
1.75	-2.341	-0.591	-1.952	-0.239	-0.837	-4.356	-2.534	-2.492
2.00	-2.457	-0.587	-2.195	-0.232	-0.860	-4.258	-2.239	-2.546
2.25	-2.834	-0.584	-2.437	-0.224	-0.899	-4.176	-1.992	-2.631
2.50	-3.082	-0.582	-2.679	-0.216	-0.956	-4.111	-1.799	-2.769

contd ...

1.	2	3	4	5	6	7	8	9
2.75	-3.330	-0.530	-2.921	-0.208	-1.028	-4.063	-1.654	-3.006
3.00	-3.578	-0.578	-3.163	-0.201	-1.115	-4.028	-1.549	-3.269
3.25	-3.827	-0.577	-3.407	-0.194	-1.211	-4.003	-1.473	-3.552
3.50	-4.075	-0.576	-3.651	-0.188	-1.315	-3.984	-1.417	-3.849
3.75	-4.325	-0.575	-3.897	-0.184	-1.424	-3.971	-1.377	-4.155
4.00	-4.574	-0.575	-4.143	-0.181	-1.534	-3.960	-1.347	-4.468
4.25	-4.824	-0.574	-4.391	-0.177	-1.654	-3.953	-1.325	-4.787
4.50	-5.074	-0.574	-4.638	-0.176	-1.772	-3.948	-1.308	-5.130
4.75	-5.323	-0.573	-4.887	-0.174	-1.855	-3.945	-1.300	-5.422
5.00	-5.573	-0.574	-5.137	-0.174	-1.855	-3.845	-1.300	-5.547

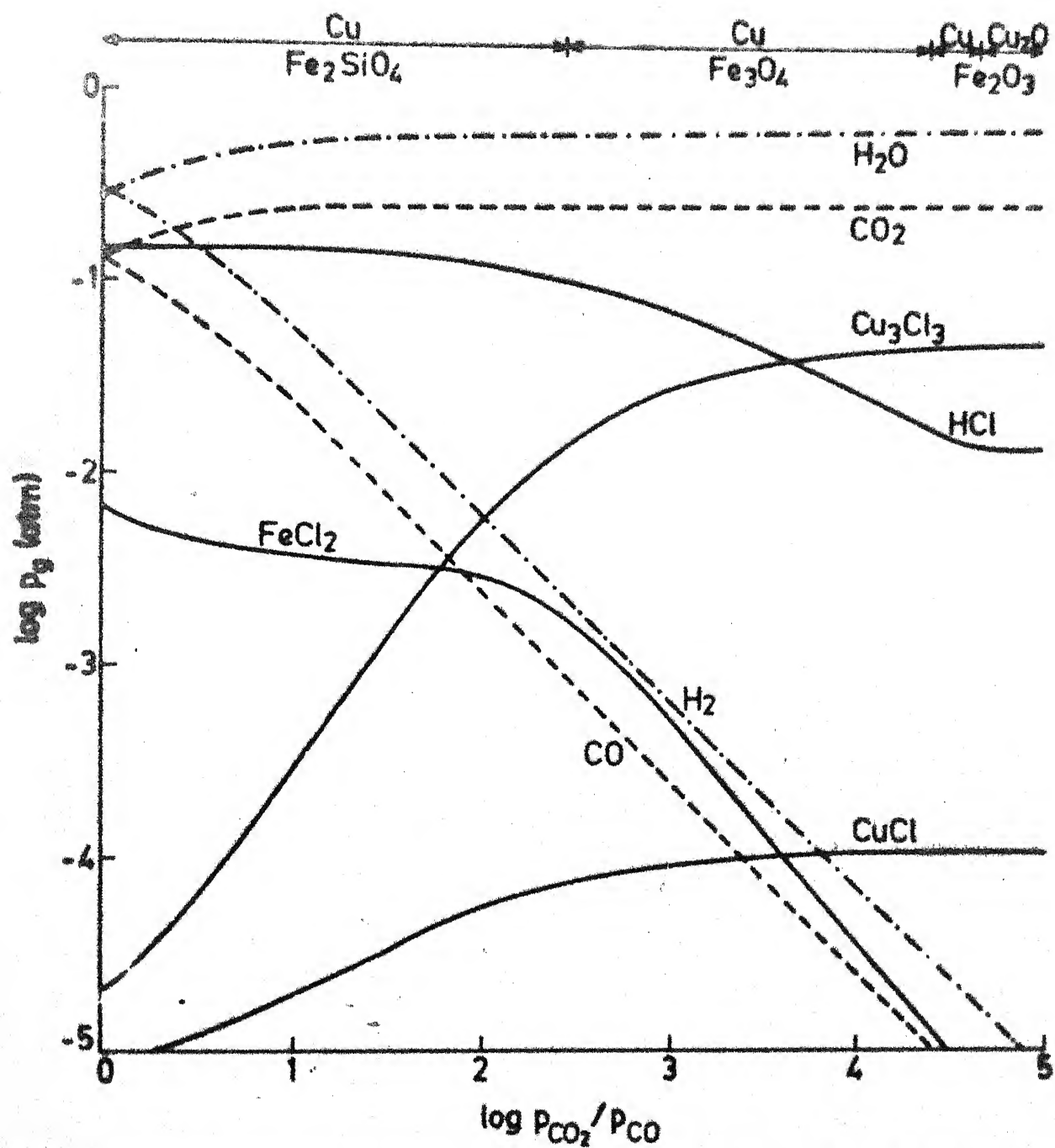


Fig.5.1 Plot of partial pressures of the various gaseous species against oxygen potential at 1100°K in copper segregation system. Amounts participating in the reaction are:

C: 0.3%, NaCl: 0.9%, H_2O : 1.14%

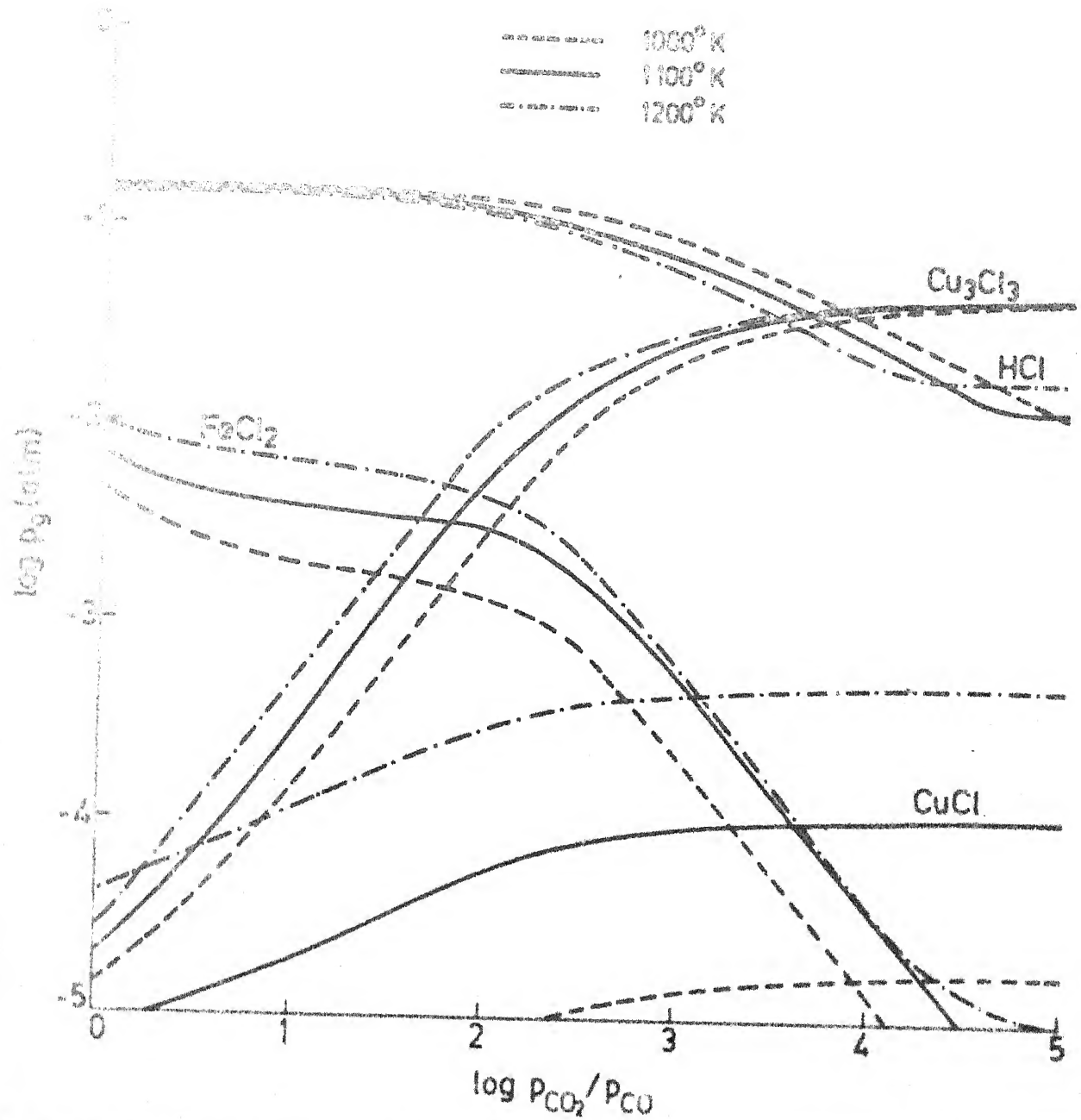


Fig. 5.2 Plot of partial pressures against oxygen potential at 1000°K, 1100°K and 1200°K. Amounts participating are the same as in Fig 5.1

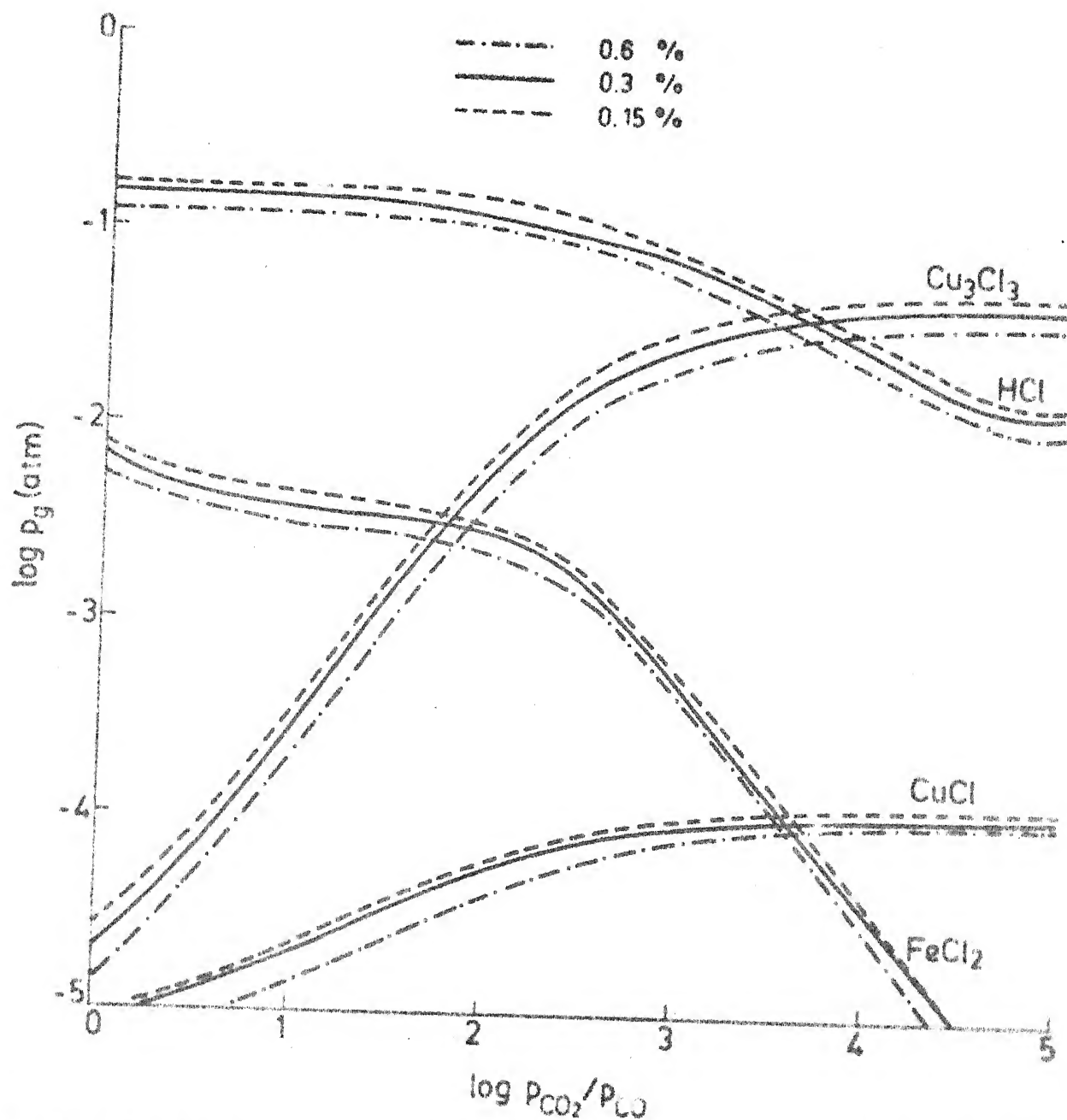


Fig.5.3 Plot of partial pressures against oxygen potential when the participating amounts of carbon varied, other conditions remaining the same as in Fig.5.1.

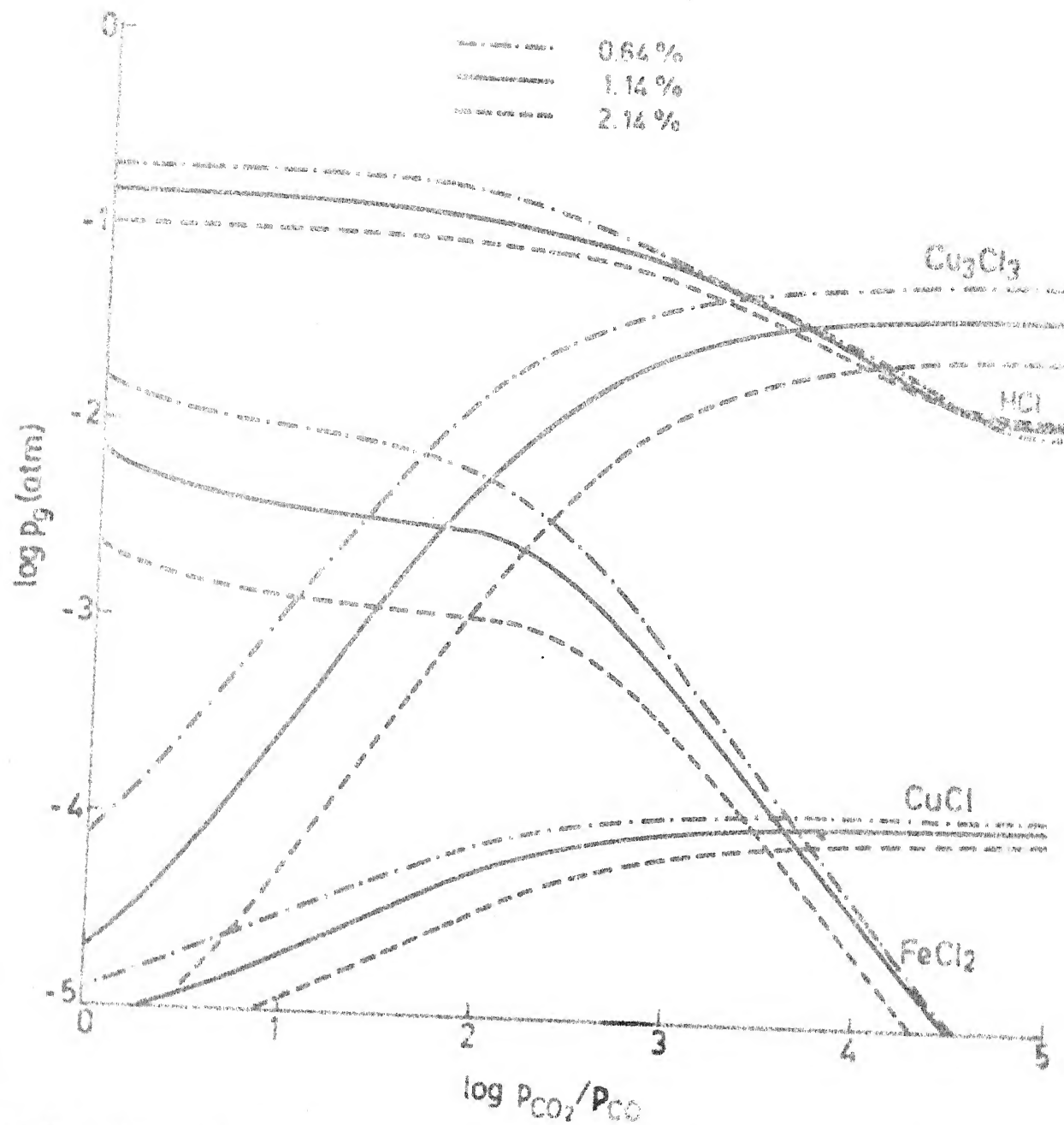


Fig 5.4 Plot of partial pressures against oxygen potential when the amounts of H_2O participating in the reaction varied, other conditions remaining the same as in Fig 5.1

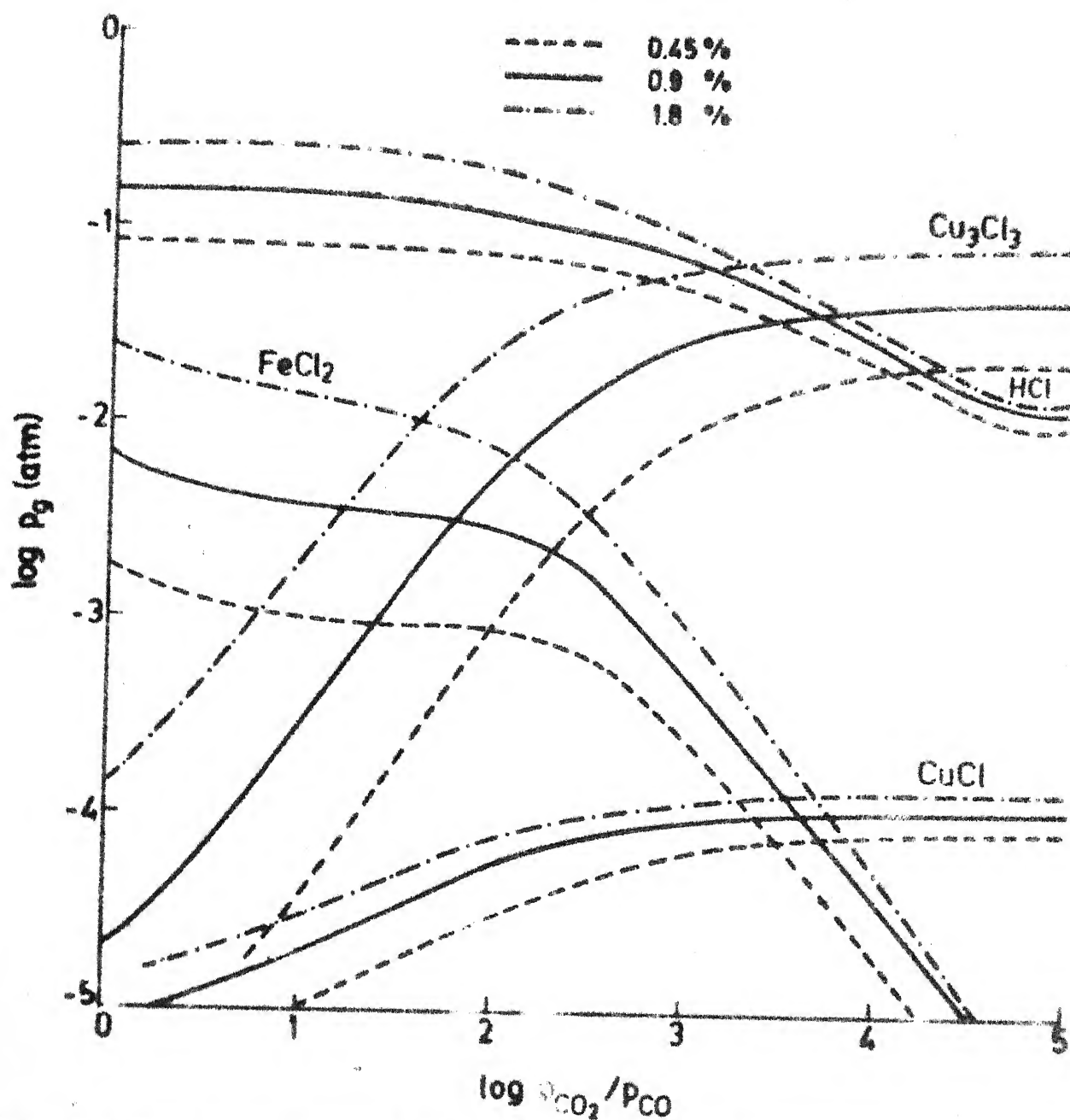


Fig. 5.5 Plot of partial pressures against oxygen potential when the participating amounts of NaCl varied, other conditions remaining the same as in Fig. 5.1

Nickel Segregation :

Calculations analogous to the one employed in the case of Cu Segregation may be carried out for the case of Nickel too. Here, a 100 g pellet constitutes 2 g Ni, 20 g Fe, 6 g CaCl_2 , 3g C with the balance as gangue. Incorporating the values of n_{C} , n_{H} , n_{Cl} and the values of K at the temperature 1200°K , the equations in the Nickel Segregation system are solved simultaneously. The results are tabulated in Table 5.2, and a plot of the partial pressures of the various gaseous species against the Oxygen potential is made in Fig. 5.6.

Contrary to the case of Cu Segregation, the predominant species are CO_2 , HCl and H_2O , with a fairly significant amount of FeCl_2 too. As in the case of Cu Segregation, the curve of NiCl_2 exhibits a sharp gradient, but without a consonant match from the profiles of HCl . The sharp fall in the NiCl_2 curve indicates that it could be transported to the carbon surface to get reduced to metallic Nickel, but the high vapor pressure of HCl at the region of higher Oxygen potential betrays this conclusion. The chloride vapors may, therefore, not be utilised in a cyclic manner for the chlorination within the pellet, leading to a larger consumption of the chloride, a fact that has been corroborated by experimental studies by a number of Research workers.

The study of the effect of various process parameters is made by varying the input composition of the reductant, chloride, water, and by varying the temperature. The results are plotted in Figs. 5.7 to 5.10. Since the Hydrogen chloride generated in the Nickel Segregation system is lost in the bulk furnace gases, impeding a cyclic reaction characteristic of Cu Segregation, the premise utilised in the Cu Segregation cannot be employed for the Nickel Segregation. However, it may be observed that the NiCl_2 partial pressure increases with increasing CaCl_2 amount, decreasing amount of participating carbon and increasing temperature.

Comparison of the Nickel and Copper Segregation systems on a broader schema indicates that Segregation reactions seem more favourable in the case of the latter than the former.

Table 5.2

Logarithmic equilibrium partial pressures of the gaseous species at varied $\log(p_{\text{CO}_2}/p_{\text{CO}})$ values at 1200°K

Ratios	CO	CO ₂	H ₂	H ₂ O	HCl	NiCl ₂	FeCl ₂
1	2	3	4	5	6	7	8
0.00	-0.466	-0.466	-1.389	-1.283	-0.819	-3.944	-1.143
0.25	-0.609	-0.359	-1.566	-1.210	-0.796	-3.720	-1.169
0.50	-0.784	-0.284	-1.768	-1.162	-0.781	-3.489	-1.188
0.75	-0.986	-0.236	-1.987	-1.131	-0.772	-3.253	-1.201
1.00	-1.206	-0.207	-2.218	-1.112	-0.767	-3.012	-1.210
1.25	-1.434	-0.189	-2.456	-1.100	-0.766	-2.770	-1.218
1.50	-1.678	-0.179	-2.698	-1.019	-0.767	-2.529	-1.228
1.75	-1.923	-0.173	-2.941	-1.085	-0.768	-2.291	-1.240
2.00	-2.169	-0.169	-3.182	-1.076	-0.774	-2.060	-1.259
2.25	-2.418	-0.168	-3.421	-1.065	-0.784	-1.842	-1.290
2.50	-2.666	-0.166	-3.682	-1.076	-0.772	-1.795	-1.326
2.75	-2.916	-0.166	-3.947	-1.090	-0.758	-1.753	-1.367
3.00	-3.165	-0.166	-4.210	-1.104	-0.745	-1.714	-1.412
3.25	-3.415	-0.165	-4.473	-1.117	-0.734	-1.679	-1.459
3.50	-3.665	-0.165	-4.735	-1.129	-0.723	-1.646	-1.510
3.75	-3.915	-0.165	-4.997	-1.141	-0.715	-1.616	-1.564
4.00	-4.165	-0.165	-5.258	-1.152	-0.707	-1.589	-1.621

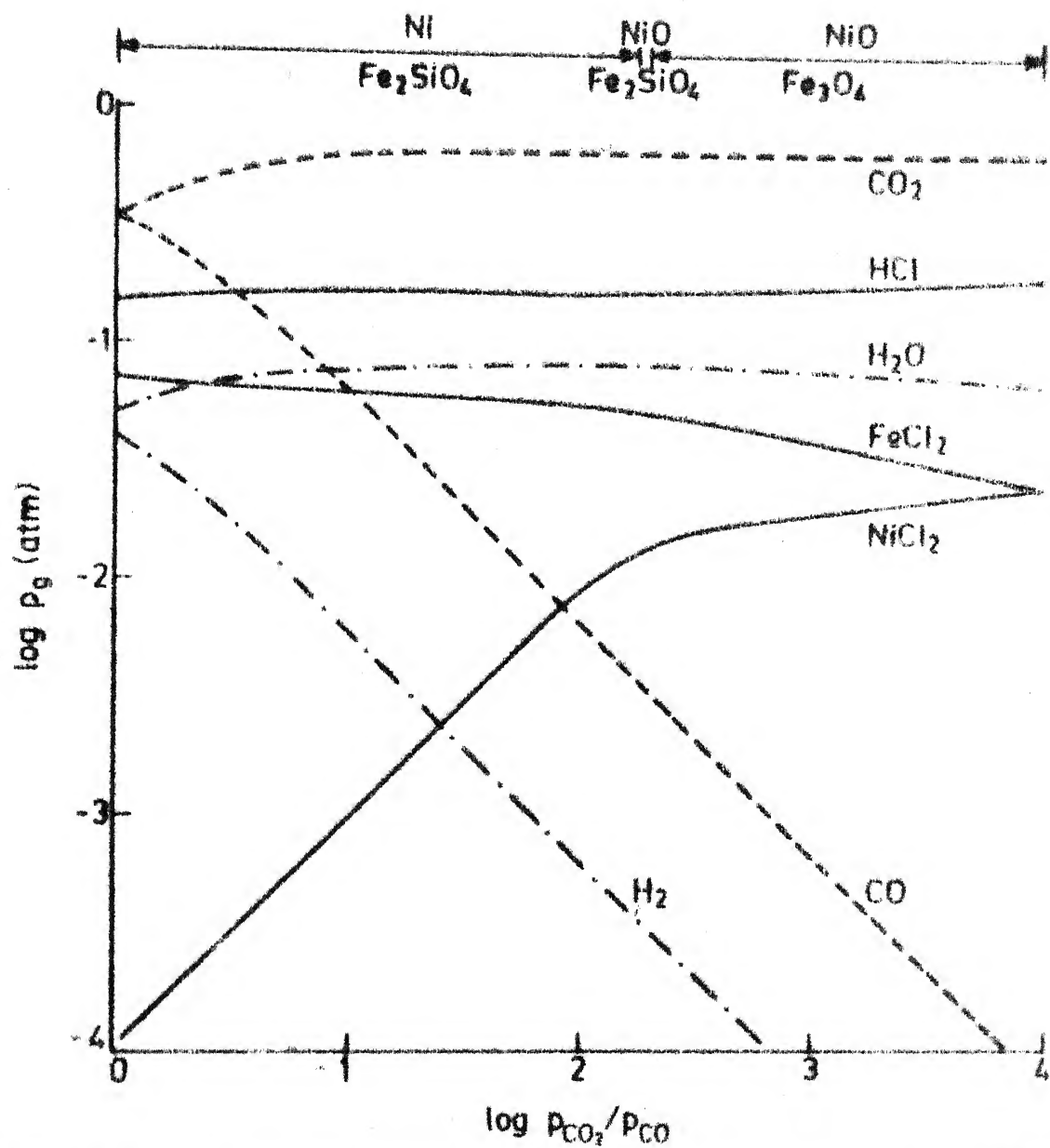


Fig. 5.6 Plot of partial pressures against oxygen potential at 1200°K in Ni segregation system. Amounts participating in the reaction are: C 1%, CaCl_2 2%, H_2O 0.37%

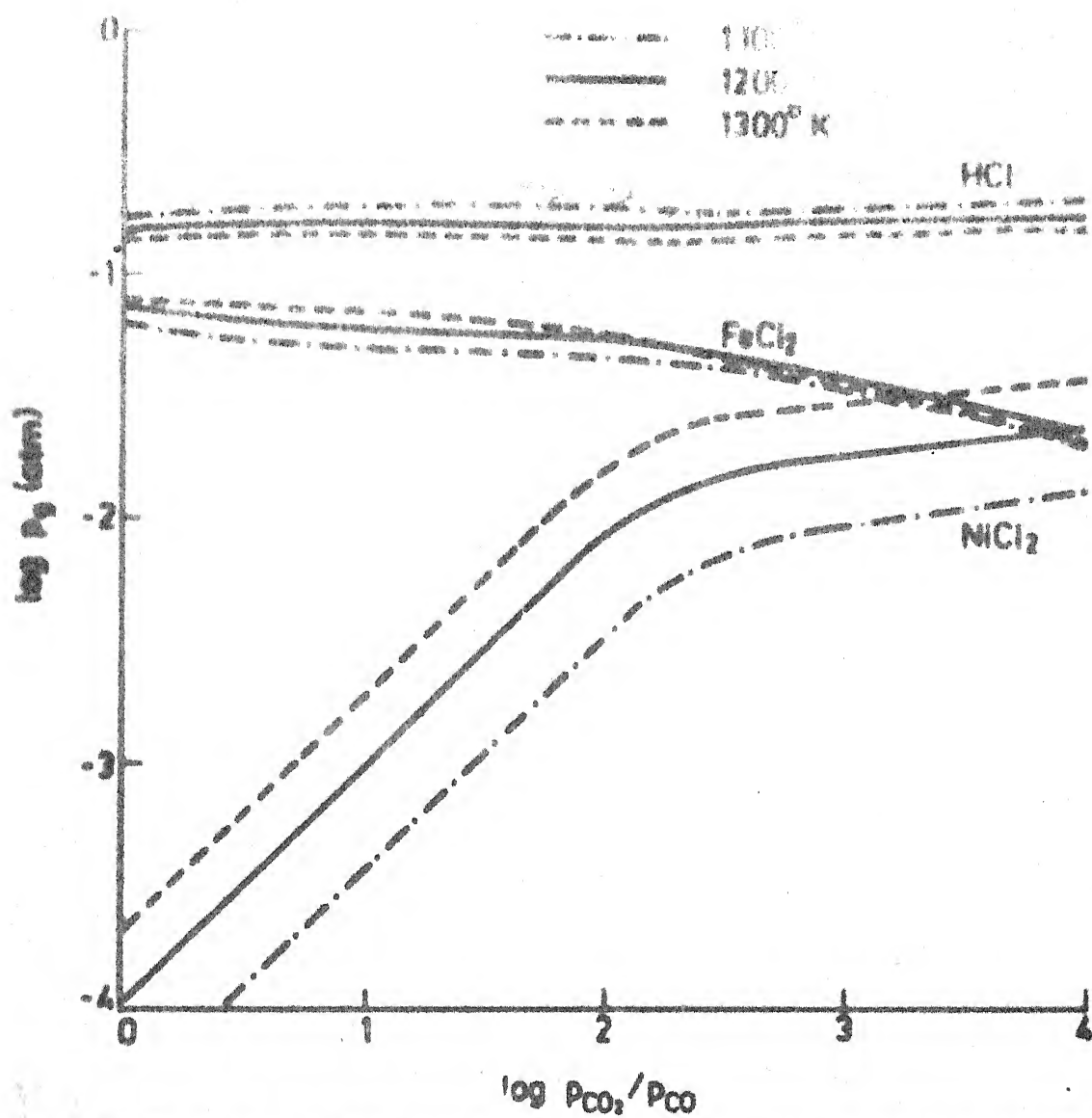


Fig. 5.7 Plot of partial pressures against oxygen potential at 1100°K, 1200°K and 1300°K. Amounts participating in the reactions are the same as in Fig. 5.6.

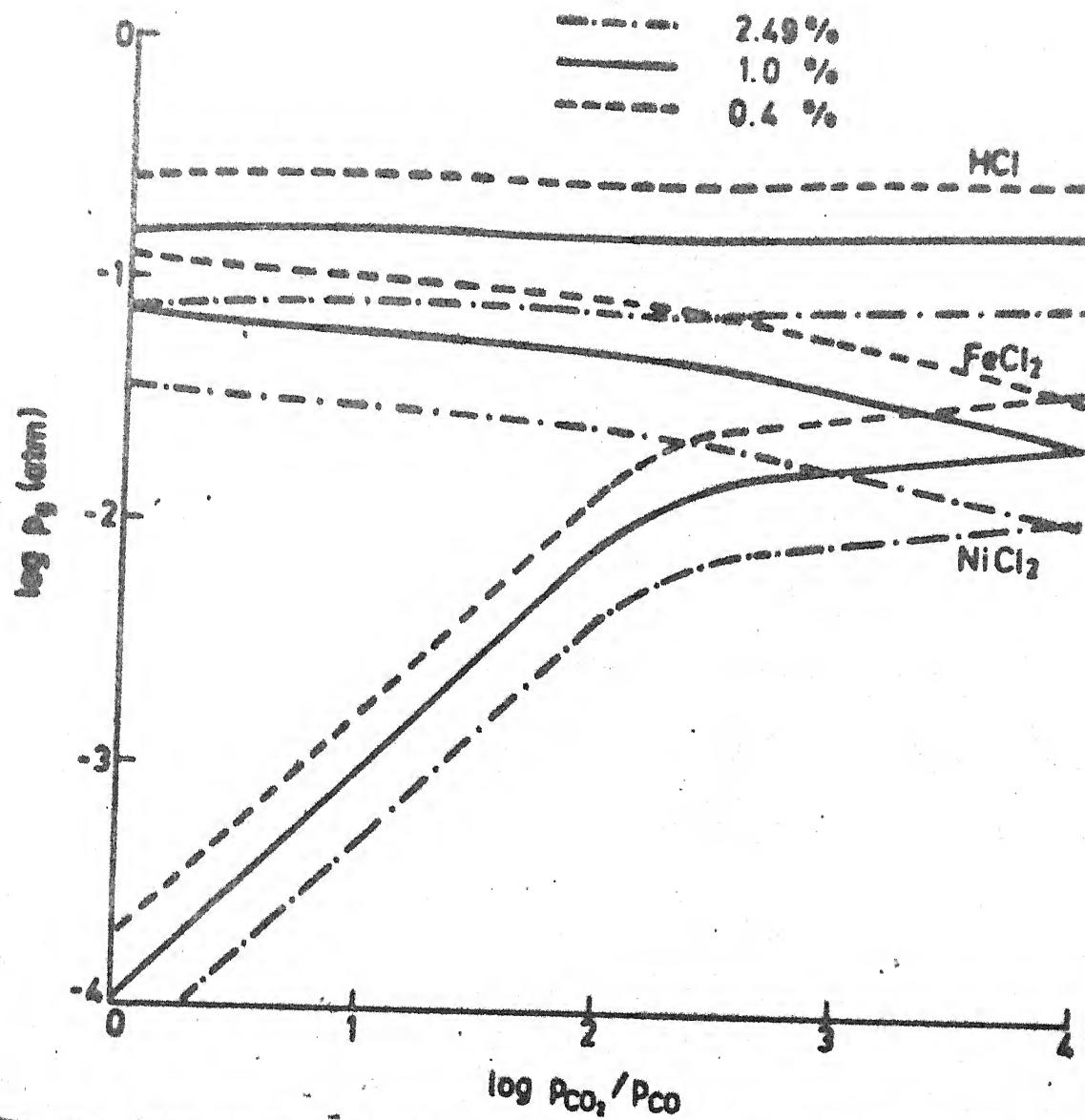


Fig. 5.8 Plot of partial pressures against oxygen potential when the participating amounts of carbon varied, other conditions remains the same as in Fig.5.6.

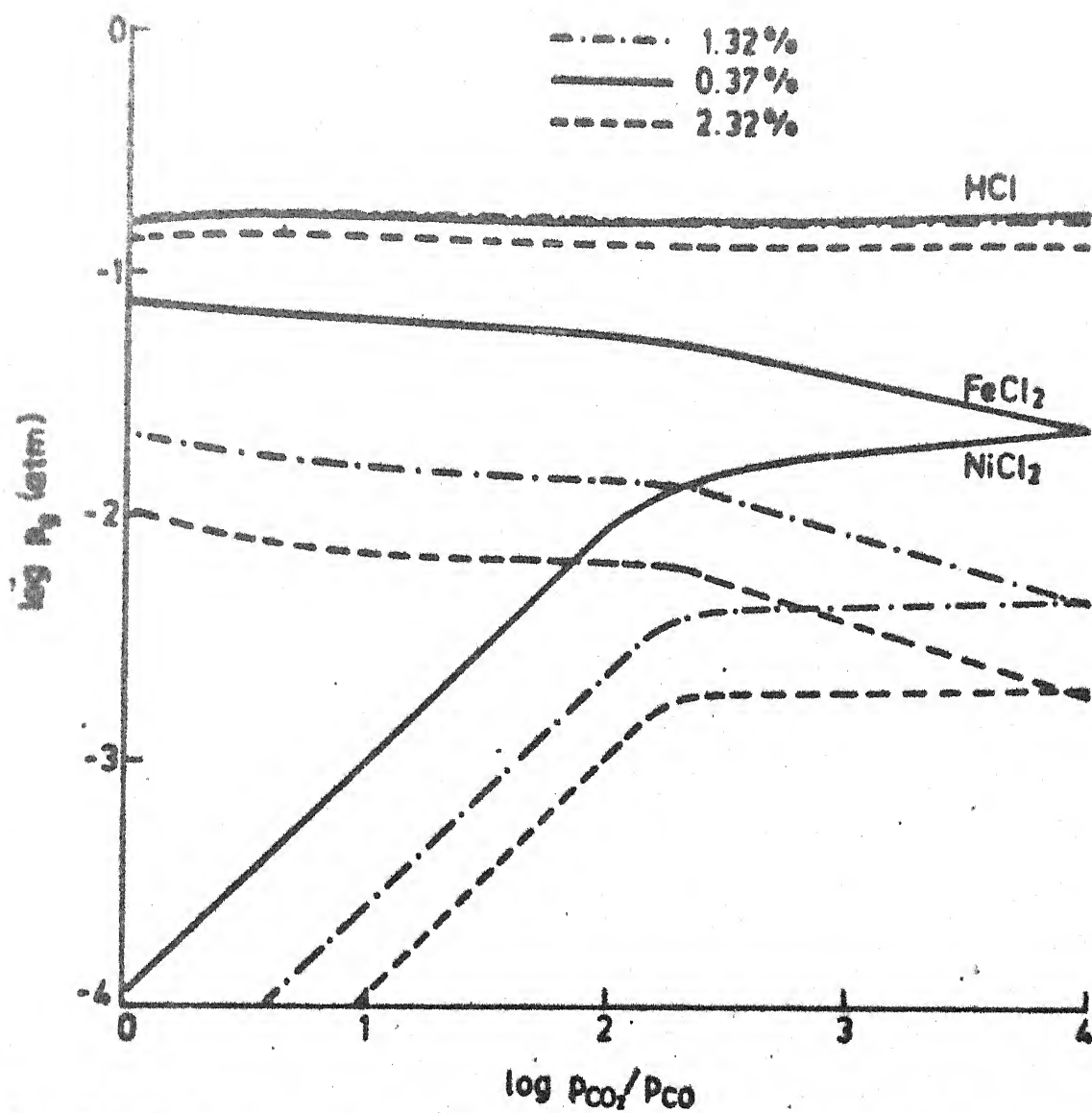


Fig. 5.9 Plot of partial pressures against oxygen potential when the participating amounts of H_2O varied, other conditions remaining the same as in Fig. 5.6.

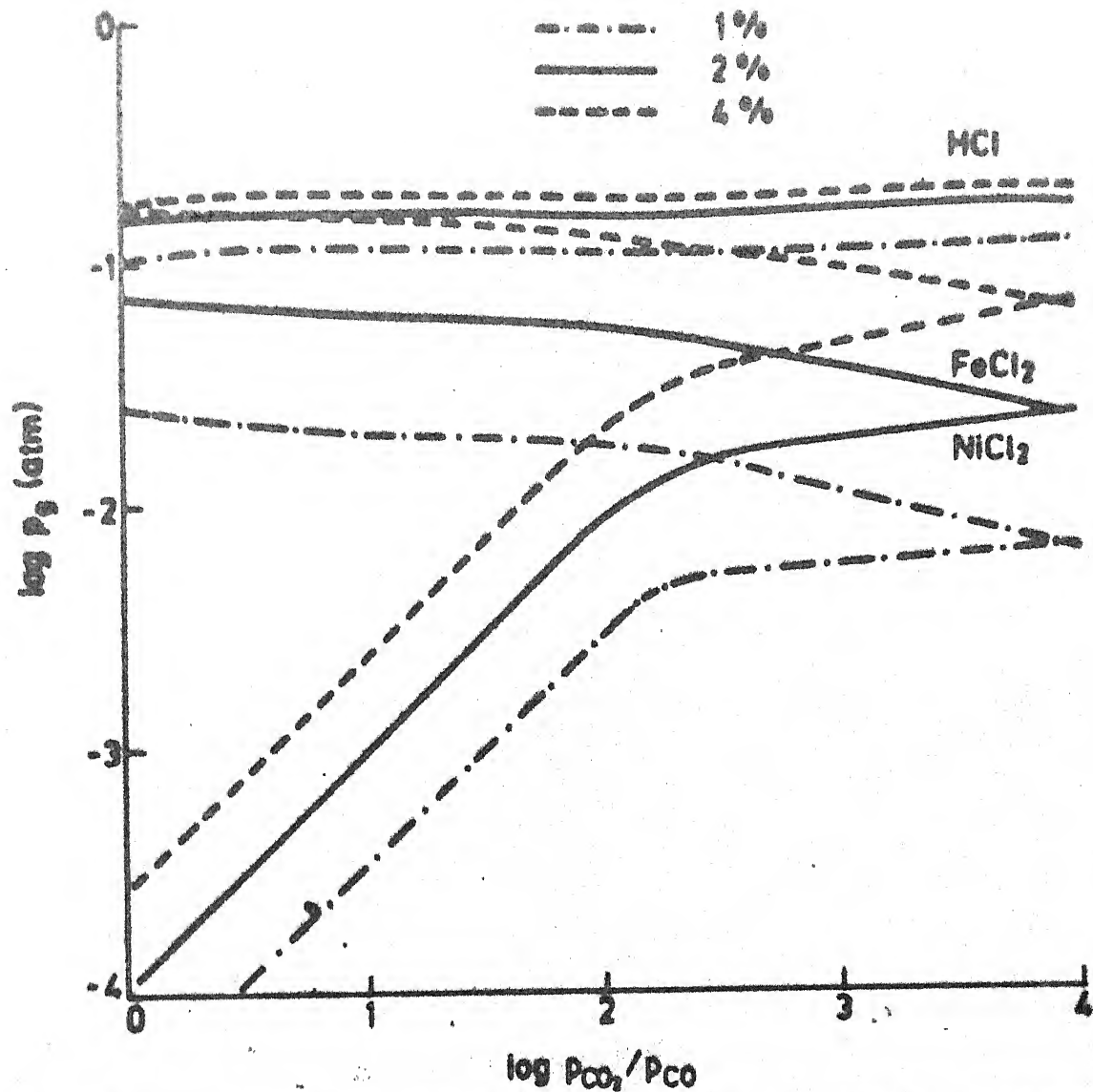


Fig. 5.10 Plot of partial pressures against oxygen potential when the participating amounts of chloride varied, other conditions remaining the same as in Fig. 5.6.

CHAPTER 6

ANALYSIS THROUGH FREE ENERGY MINIMISATION TECHNIQUES

In a closed, chemically reacting system at constant pressure and temperature, the potential function which governs chemical changes is the Gibbs free energy. The condition for chemical equilibrium is that the free energy must be a minimum. The free energy minimisation technique is based on this principle (32-34,42).

In the present study, thermodynamic calculation were carried out on the system Cu-Fe-C-H-Cl-O using the Free energy Minimisation technique. At a given temperature and pressure, the free energies of all possible mixtures of a given set of species form a surface in the hyper space, the coordinates of which are the species, certain areas on this surface cannot be realised due to the mass balance constraint not being satisfied, The objective then is to find that location on the accessible areas where the free energy is a minimum. The set of coordinates, or mole fractions, that define the minimum point constitute the desired equilibrium composition.

Formulation :

The total free energy of a mixture of gaseous and condensed species can be expressed as :

$$F^* = RT \sum_{i=1}^n f_i^g + \sum_{j=1}^m f_j^s \quad (6.1a)$$

Thus, the free energy function

$$F(x) = \frac{F^*(X)}{RT} = \sum_{i=1}^n f_i^G + \sum_{j=1}^m f_j^S \quad (6.1b)$$

where,

X is the set formed by the mole numbers of all the species

$$X = (X_1^G, X_2^G, \dots, X_n^G; X_1^S, X_2^S, \dots, X_m^S),$$

$$f_i^G = X_i^G (C_i^G + \ln \frac{X_i^G}{\bar{X}}),$$

$$\bar{X} = \sum_{i=1}^n X_i^G$$

$$C_i^G = \frac{F}{RT} |_i^G + \ln P$$

$$f_j^S = X_j^S C_j$$

$$C_j^S = \frac{F}{RT} |_j^S$$

For obtaining the equilibrium composition, a set of positive mole numbers, satisfying the mass balance and minimising the total free-energy, are to be generated. At constant temperature minimization of free energy is equivalent to minimizing the free energy function F . The mass balance constraint can be written as

$$\sum_{i=1}^n a_{ie}^G x_i^G + \sum_{j=1}^m a_{je}^S x_j^S = b_e \quad (6.2)$$

for $e = 1, 2, \dots, NE$

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where b_o = elemental abundances

NE = number of elements.

Let Y be an initial guess for the mole numbers of gaseous and condensed species, such as

$$Y = (Y_1^g, Y_2^g, \dots, Y_n^g ; Y_1^s, Y_2^s \dots Y_m^s)$$

Let Y be a positive set satisfying the mass balance constraint

The free energy expression for this composition is

$$F(Y) = \sum Y_i^g (C_i^g + \ln \frac{Y_i^g}{\bar{Y}}) + \sum_{j=1}^m Y_j^s C_j^s$$

where $\bar{Y} = \sum_{i=1}^n Y_i^g$

Let Δ be the difference between X and Y so that

$$\Delta_i^g = X_i^g - Y_i^g$$

$$\Delta_j^s = X_j^s - Y_j^s$$

$$\Delta' = \bar{X} - \bar{Y}$$

By expanding $F(X)$ about Y using Taylor's series (and neglecting higher order terms) $\phi(X)$ can be obtained

$$\begin{aligned}
\phi(X) = & F(Y) + \sum \frac{\partial F}{\partial X_i^g} \Big|_{X=Y} \Delta_i^g + \sum \frac{\partial F}{\partial X_j^s} \Big|_{X=Y} \Delta_j^s \\
& + \frac{1}{2} \sum_{i=1}^n \sum_{k=1}^n \frac{\partial^2 F}{\partial X_i^g \partial X_k^g} \Big|_{X=Y} \Delta_i^g \Delta_k^g \\
& + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^m \frac{\partial^2 F}{\partial X_i^g \partial X_j^s} \Big|_{X=Y} \Delta_i^g \Delta_j^s \\
& + \frac{1}{2} \sum_{j=1}^m \sum_{g=1}^m \frac{\partial^2 F}{\partial X_j^s \partial X_g^s} \Big|_{X=Y} \Delta_j^s \Delta_g^s
\end{aligned} \tag{6.4}$$

Among the derivatives,

$$\frac{\partial F}{\partial X_i^g} = C_i^g + \ln \frac{X_i^g}{\bar{X}}$$

$$\frac{\partial F}{\partial X_j^s} = C_j^s$$

$$\frac{\partial^2 F}{\partial X_i^g \partial X_k^g} = \begin{cases} \frac{1}{X_i^g} - \frac{1}{\bar{X}} & \text{if } i = k \\ -\frac{1}{\bar{X}} & \text{if } i \neq k \end{cases}$$

and

$$\frac{\partial^2 F}{\partial X_i^g \partial X_j^s} = \frac{\partial^2 F}{\partial X_j^s \partial X_g^s} = 0$$

Substituting these derivatives in (6.4)

$$\begin{aligned} \phi(X) = F(Y) + \sum_{i=1}^n (C_i^g + \ln \frac{Y_i^g}{\bar{Y}}) \Delta_i^g \\ + \sum_{j=1}^m C_j^s \Delta_j^s + \frac{1}{2} \sum_{i=1}^n Y_i^g \left[\frac{\Delta_i^g}{Y_i^g} - \frac{\Delta_i^g}{\bar{Y}} \right]^2 \end{aligned} \quad (6.5)$$

$\phi(X)$ is to be minimised subject to the side constraint of mass balance equations (6.2). Now, another function $L(X)$ may be defined combining (6.5) and (6.2) using Lagrangian multipliers

μ_e

$$L(X) = \phi(X) + \sum_e \mu_e [b_e - \sum_{i=1}^n a_{ie}^g X_i^g - \sum_j a_{je}^s X_j^s] \quad (6.6)$$

Now to minimise this function,

$$\frac{\partial L(X)}{\partial X_i^g} = \frac{\partial L(X)}{\partial X_j^s} = 0$$

The change of free energy with a change in moles of gaseous species becomes

$$\frac{\partial L(X)}{\partial X_i^g} = [C_i^g + \ln \frac{Y_i^g}{\bar{Y}}] + \left[\frac{X_i^g}{Y_i^g} - \frac{\bar{X}}{\bar{Y}} \right] - \sum_e \mu_e a_{ie}^g = 0 \quad (6.7)$$

Similarly, for solids,

$$\frac{\partial L(X)}{\partial X_j^s} = C_j^s - \sum_e \mu_e a_{je}^s = 0 \quad (6.8)$$

Obtaining X_i^g from (6.7)

$$X_i^g = -Y_i^g [C_i^g + \ln \frac{Y_i^g}{\bar{Y}}] + Y_i^g [\frac{\bar{X}}{\bar{Y}}] + \sum_{e=1}^{NE} [\mu_e a_{ie}^g] Y_i^g \quad (6.9)$$

Summing (6.9) over i for all gases,

$$\sum_{e=1}^{NE} \mu_e \sum a_{ie}^g Y_i^g = \sum (C_i^g + \ln \frac{Y_i^g}{\bar{Y}}) Y_i^g \quad (6.10)$$

$$\text{Let } r_{ek} = r_{ke} = \sum_{i=1}^n (a_{ie}^g a_{ik}^g) Y_i^g$$

for $e, k = 1, 2, \dots, NE$

By substituting (6.9) in (6.2), NE number of equations are obtained. These equations together with (6.8) and (6.10) form a set of $(NE+m+1)$ linear equations, for the unknowns : μ_e (Lagrangian multipliers) mole numbers of solid species $X_1^s, X_2^s, \dots, X_m^s$ and the value of \bar{X}/\bar{Y} .

The set of equations to be solved are :

$$\begin{aligned} \beta_1(\bar{X}/\bar{Y}) + a_{11}^s X_1^s + a_{21}^s X_2^s + \dots + a_{m1}^s X_m^s + r_{11} \mu_1 + \dots + r_{1NE} \mu_{NE} &= \\ b_1 + \sum_i a_{i1}^g f_i^g & \\ \beta_2(\bar{X}/\bar{Y}) + a_{12}^s X_1^s + a_{22}^s X_2^s + \dots + a_{m2}^s X_m^s + r_{21} \mu_1 + \dots + r_{2NE} \mu_{NE} &= \\ b_2 + \sum_i a_{i2}^g f_i^g & \\ \vdots & \\ \beta_{NE}(\bar{X}/\bar{Y}) + a_{1NE}^s X_1^s + \dots + a_{mNE}^s X_m^s + r_{NE1} \mu_1 + \dots + r_{NENE} \mu_{NE} &= \\ b_{NE} + \sum_i a_{iNE}^g f_i^g & \end{aligned}$$

$$\beta_1 \mu_1 + \beta_2 \mu_2 + \dots + \beta_{NE} \mu_{NE} = \Sigma f_i^g \quad (6.12)$$

$$a_{11}^s \mu_1 + a_{12}^s \mu_2 + \dots + a_{1NE}^s \mu_{NE} = C_1^s \quad (6.13)$$

$$a_{21}^s \mu_1 + a_{22}^s \mu_2 + \dots + a_{2NE}^s \mu_{NE} = C_2^s$$

$$\vdots \quad \quad \quad \vdots \quad \quad \quad \vdots$$

$$a_{m1}^s \mu_1 + a_{m2}^s \mu_2 + \dots + a_{mNE}^s \mu_{NE} = C_m^s$$

$$\text{where } \beta_e = \sum_{i=1}^n a_{ie}^g X_i^g.$$

The solution to the set of equations (6.11), (6.12) and (6.13) give a new approximation for the condensed species. The values of β_e , μ_e and (\bar{X}/\bar{Y}) when substituted into (6.9) yields the new values of X_i^g . By repeating this process, the final equilibrium value is reached. The method of steepest descent was used to facilitate ultimate convergence; this was defined to have been reached when the sum of the absolute values of the changes in mole fractions between the subsequent iterations was $< 10^{-5}$.

Analysis of $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{C}-\text{HCl}$ System

The input composition of the components chosen was the one typically encountered in the segregation process of Oxide Copper Ores. From this, the elemental abundances are given by

$$b_{\text{Cu}} = 2 \cdot x_{\text{Cu}_2\text{O}}$$

$$b_{\text{Fe}} = 2 \cdot x_{\text{Fe}_2\text{O}_3}$$

$$b_{\text{C}} = x_{\text{C}}$$

$$b_{\text{Cl}} = x_{\text{HCl}}$$

$$b_{\text{O}} = 3 x_{\text{Fe}_2\text{O}_3} + x_{\text{Cu}_2\text{O}}$$

where x_i represents the mole fraction of the input species i .

The gaseous species, the condensed species and the elements in the system are to be specified initially. The elements in the system are Cu, Fe, C, H, Cl, O. The free energy data of all the Chemical species conceivable in the system, at the temperature and the pressure considered, are to be specified. These were obtained from the JANAF tables⁽³⁰⁾.

A number of gaseous species were considered in the system. These include CuCl, Cu₃Cl₃, FeCl, FeCl₂, FeCl₃, Fe₂Cl₆, CO, CO₂, H₂, H₂O, HCl, O₂, Cl₂, O. From the partial pressures of the gaseous species so resulting, that have been tabulated in Table 6.1, only the following were significant : Cu₃Cl₃, CuCl, FeCl₂, H₂, H₂O, CO₂, CO, HCl. The condensed species that were considered at equilibrium were Cu, C and Fe₂O₃.

The following test may be conducted for the presence of solid phases. For each of the solids, if the quantity

$$[(F/RT)_j - \sum \mu_e a_{je}^s] \quad (6.14)$$

is less than zero, then that particular solid is to be incorporated into the calculation.

Results and Discussion :

With the input composition of (in mole fractions) Cu₂O = 0.06, Fe₂O₃ = 0.73, C = 0.16 and HCl = 0.05, the final equilibrium composition of the gaseous species and the

Table 6.1

Equilibrium mole fractions of the chemical species
at 1100°K and input ingredients of $\text{Cu}_2\text{O}:0.06, \text{Fe}_2\text{O}_3:0.73,$
 $\text{C}:0.16, \text{HCl}:0.05$

So Sl. No.	Chemical species	Mole fractions
1.	CuCl(g)	0.1655×10^{-6}
2.	$\text{Cu}_3\text{Cl}_3\text{(g)}$	0.289×10^{-7}
3.	FeCl(g)	0.162×10^{-10}
4.	$\text{FeCl}_2\text{(g)}$	0.156×10^{-1}
5.	$\text{FeCl}_3\text{(g)}$	0.134×10^{-7}
6.	$\text{Fe}_2\text{Cl}_6\text{(g)}$	0.634×10^{-11}
7.	CO(g)	0.747×10^{-1}
8.	$\text{CO}_2\text{(g)}$	0.446×10^{-2}
9.	$\text{H}_2\text{(g)}$	0.147×10^{-1}
10.	$\text{H}_2\text{O(g)}$	0.887×10^{-3}
11.	HCl(g)	0.205×10^{-2}
12.	$\text{O}_2\text{(g)}$	0.693×10^{-21}
13.	$\text{Cl}_2\text{(g)}$	0.659×10^{-13}
14.	O(g)	0.218×10^{-19}
15.	Cl(g)	$0.134 \times 10^{-}$
16.	Cu(s)	0.12213
17.	C(s)	0.765×10^{-1}
18.	$\text{Fe}_2\text{O}_3\text{(s)}$	0.689

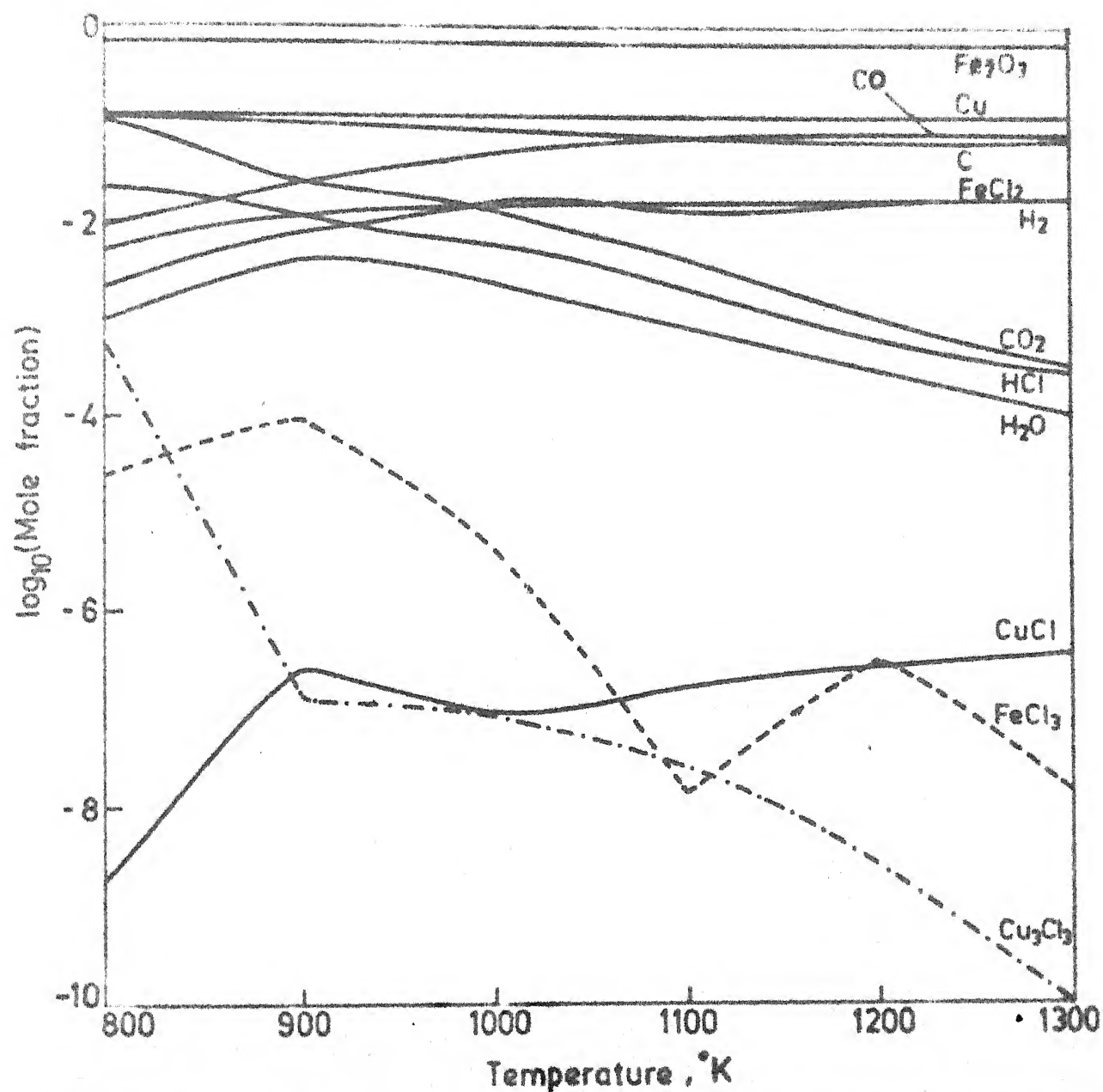


Fig. 6.1 Plot of equilibrium mole fractions of the chemical species as a function of temperature. (Starting $\text{Cu}_2\text{O} = 0.06$, $\text{Fe}_2\text{O}_3 = 0.73$, $\text{C} = 0.16$, $\text{HCl} = 0.05$)

condensed species were computed by the free energy minimisation technique at a temperature range varying from 800°K to 1300°K . The results indicate that a highly reducing atmosphere prevails in the system, and all the Oxide Copper gets reduced to Copper. The test for the presence of Cuprous as well as Cupric oxide failed to yield positive results. The test indicated the likelihood of Fe_3O_4 , FeO and Fe which have to be incorporated in future work to check for certain the presence of any of these condensed species.

A plot of the logarithmic value of the mole fractions of the chemical species at equilibrium as a function of temperature is shown in Fig. 6.1. Among the gaseous species present in significant amounts, CuCl , FeCl_3 and Cu_3Cl_3 exerted relatively lower vapor pressures. The vapor pressures of Cu_3Cl_3 and HCl increased with decrease of temperature. The amount of copper extracted predicted from the analysis at equilibrium did not show significant perturbation with temperature, although from a strictly numerical viewpoint Cu extraction seemed to enhance with increasing temperature. Thus while the behaviour of HCl with temperature variation is identical to the one obtained by Yazawa⁽²⁾, the conclusion that an increase in the partial pressure of HCl automatically meant enhanced segregation is not in confirmity with the results obtained here which show higher vapour pressures of HCl coupled with lower amounts of copper (albeit relative differences in their amounts being

very small). Before drawing definite conclusions, the input compositions may have to be varied, and all possible condensed species included in the analysis to simulate the situation in a segregation system. Analysis of the 7 component system Cu-Fe-Si-C-H-Cl-O to take care of the presence of SiO_2 in the Ore would be useful.

CHAPTER 7

LABORATORY SCALE SEGREGATION ROASTING

Laboratory Scale Experiments on Segregation Roasting of synthetic Copper Ore were designed to assess the effect of the various process variables on the extraction of copper. Synthetic Copper Ore with varying contents of the oxide of copper were employed.

Equipment and Test Procedure :

A miniature sketch (not to scale) of the Segregation apparatus that was finally used in the laboratory is available in Fig. 7.1, the previous attempts at using a 20 mm dia, 75 cm long Quartz tube^{and} an Alumina tube having lead to their breakage due to exposure to high temperature and moisture. The body of the apparatus is of stainless steel, 30 mm dia and 200 mm long. Two tubes of 3 mm and 6 mm dia are welded to one of the flanges, the former for carrying the moisture, and the latter to introduce the thermocouple as also to act as the outlet of the outgoing gases.

A schematic sketch of the set-up for lab scale segregation experiments is shown in Fig. 7.2. Argon is purified by passing it through copper gauze maintained at 200-300°C in a tube furnace, and then allowed to bubble through a water saturator at room temperature to provide water vapor in the sample atmosphere.

In the laboratory scale studies, a modification of the experimental practice employed by Opie et al⁽¹¹⁾ was used for the treatment of 50g samples of synthetic Ore. In this method, which is especially useful due to the small amount of synthetic Ore utilised, the copper coated carbon fraction of the treated charge is separated from the rest of the product by screening on a ASTM 60 mesh sieve. The appropriate sizing of the carbon originally added to the reaction charge makes this possible. Initially Segregation on Oxide Copper Ore was attempted, but had to be abandoned due to the extremely low amount of Cu in the Ore (0.3% Cu) that lead to difficulties in analysis of the sample after Segregation Roasting. Thus a synthetic Ore constituting Cu_2O (5%-10%), Fe_2O_3 (10%-20%) and rest SiO_2 was employed for the lab scale studies.

For each test, samples of the synthetic Ore, ground to minus 100 mesh were mixed with additions of the requisite amount of sodium chloride, and desired amount of coke, sized to minus 35 plus 50 mesh; the mixture as specified in Table 7.1 was introduced into the apparatus, and the latter placed in the Tube furnace (6.3 cms dia and 44 cms long), maintained at the desired temperature (700-750°C). Argon bubbled through the water saturator provided the moisture, and the Chromel-Alumel thermocouple introduced through the 6 mm dia tube aided in recording the temperature. The sample was Segregation roasted for 1 to 5 hours, at the end of which the apparatus was

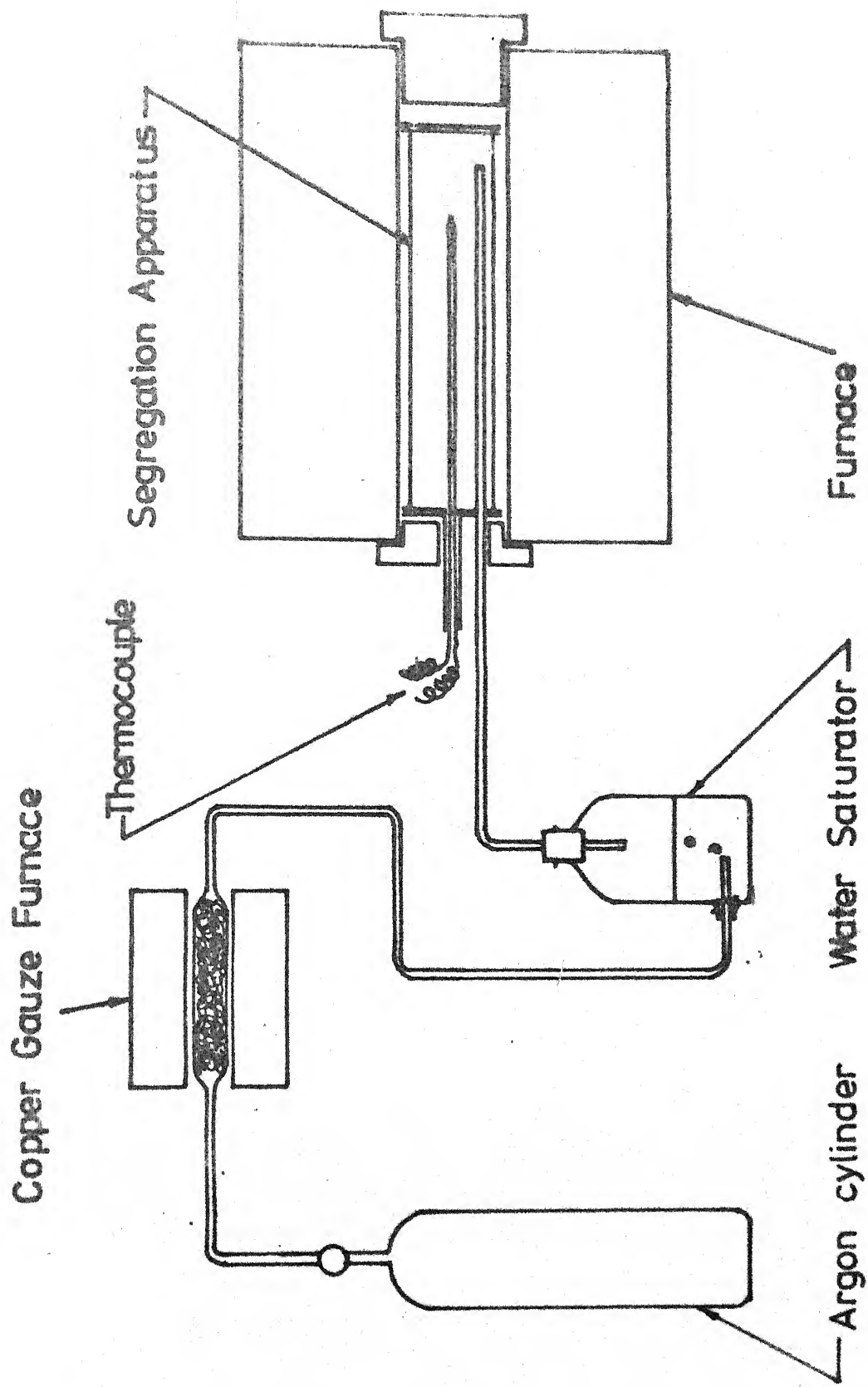


Fig. 7.1 Schematic diagram of Labscale Segregation Experiment

Table 7.1

Representative results of the laboratory scale Segregation experiments

Sl.No.	Nature of starting material	Reductant (Coke %)	Salt (NaCl %)	Moisture	Temp (°C)	Remarks
1	2	3	4	5	6	7
a) Experiments using Refractory crucible in a Muffle furnace						
1.	Natural Ore (0.3% Cu, 1.83% Fe)	1.0	0.5	Added before roasting	800	No Segregation
2.	-do-	1.5*	1.0	-do-	900	No Segregation
3.	-do-	5.0	1.0	-do-	800	No Segregation
4.	Ore Pellet	5.0	1.0	-do-	800	No Segregation
5.	Natural Ore	5.0	1.0	-do-	800	Flotation failed. Use of Natural Ore abandoned due to small amount of Copper
6.	Synthetic Ore (5% Cu ₂ O, 20% Fe ₂ O ₃ Rest SiO ₂)	1.0	0.5	-do-	800	Formed minute pellets retained the original color. No apparent Segregation

1	2	3	4	5	6	7
7.	Synthetic Ore (5% Cu ₂ O, 20% Fe ₂ O ₃ , SiO ₂)	1.0	0.5	Added before roasting	900	Formed pellets Sample was burnt (turned black)
b) Experiments with Quartz tube in tube furnace						
8.	Synthetic Ore (10% Cu ₂ O, 20% Fe ₂ O ₃ rest SiO ₂)	1.0	0.5	Argon bubbled through H ₂ O	700	No apparent Cu Segrega- tion
9.	Synthetic Ore (5% Cu ₂ O, 20% Fe ₂ O ₃ rest SiO ₂)	1.0	0.5	-do-	800	Breakage of Quartz tube
.c) Experiments with Alumina tube in tube furnace						
10.	Synthetic Ore (5% Cu ₂ O, 20% Fe ₂ O ₃ rest SiO ₂)	1.0	0.5	Argon bubbled through water	800	No apparent Copper Segre- gation
11.	-do-	1.0	0.5	Steam passed	800	Breakage of Alumina tube

1	2	3	4	5	6	7
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d) Experiments with stainless steel reactor

12.	Synthetic Ore (5% Cu ₂ O, 20% Fe ₂ O ₃ rest SiO ₂)	1.0	0.5	Argon bubbled through water	800	No apparent Cu Segregation
13.	-do-	1.0**	0.5	-do-	800	No Cu Segregation
14.	-do-	1.0	0.5	Passed steam	800	No Cu Segregation
15.	-do-	5.0	1.0	Argon through water for 2 hours	700	Color remained the same
16.	Sample of (15) roasted again	5.0	1.0	Argon bubbled for 4 hours	725	Sample turned black X-ray analysis revealed good Segregation
17.	Synthetic Ore (5% Cu ₂ O, 20% Fe ₂ O, rest SiO ₂)	5.0	1.0	Argon bubbled through water for 3 hours	725	Analysis revealed faint Segregation
18.	-do-	5.0	1.0	Argon bubbled for 5 hours	750	Light green tinge. Best Segregation results

* Fine Coal

** Activated Charcoal

removed from the furnace, cooled to room temperature under the atmosphere gas, before being removed for chemical analysis.

Results :

Screening of the treated charge on a 60 mesh sieve resulted in separation of segregate, composed of coke particles coated with copper metal, from a fine oxide residue. The segregate is made of relatively spherical particles of coke coated with spongy deposits of metallic copper. The plus 60 mesh portion was subjected to X-ray analysis to check for the presence of copper.

Under the conditions specified, X-ray analysis indicated the presence of pure metallic copper. Examination of the residual - 60 mesh portion too to X-ray analysis showed that small amount of spongy copper broke off and passed through the sieve. Such fine particles would be generally recovered as part of the segregate when flotation-separation is employed.

The best results in the lab scale segregation experiments were obtained with a mixture consisting of 1% NaCl, 5% coke and bubbling of Argon through water saturator at the rate of 60 drops per minute.

Further work, as planned during the start of the present study, could not be pursued owing to the snag involved in a thorough quantitative analysis of the segregate.

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Theoretical and experimental studies in the present work showed that :

- 1) Qualitatively speaking, Segregation is more favourable in the case of copper than Nickel.
- 2) Brown's and Powell's methods when employed even with poor initial estimates lead to the solution of the system of the simultaneous nonlinear algebraic equations, characterising the segregation system.
- 3) From a thermodynamic standpoint, copper segregation is enhanced by decreasing the temperature, decreasing the amount of water and increasing the amount of NaCl.

The analysis reveals that the partial pressure of NiCl_2 increases with increasing temperature, increasing CaCl_2 amount, and decreasing the amount of carbon.

- 4) Synthetic Ores may be employed in laboratory scale experiments for investigating the effect of the process variables in the segregation process. Synthetic Cu Ore used in the present study responded to segregation (with the modified sizing analysis employed.)

- 5) Application of a generalised computational scheme through the minimisation of Gibbs Energy to the Cu segregation system yielded the equilibrium composition of the chemical species. The technique is particularly useful due to its inherent ability to calculate the equilibrium amounts of the condensed species. This is utilised to predict the influence of various process parameters on the segregation of Copper .

Suggestion for Future work :

1. The algorithms of Brown and Powell may be applied for a thermodynamic study of the systems involving complex chemical equilibria . A check on the rigidity of the algorithms may be undertaken by
/employing a varied range of initial estimates of the unknowns.
2. The effect of a number of process parameters including temperature, nature of the reductant, salt, presence of moisture, silica, time, Ore impurities, etc. may be studied by employing a synthetic Ore to obtain an insight into the mechanism of the process.
3. The equilibrium mole fractions of the chemical species calculated by the minimisation of Free energy may be compared with the actual experimental results to obtain the efficiency of extraction of the segregated metal.

4. A number of process parameters may be varied, and its effect at the final equilibrium situation may be ascertained theoretically by the Free energy minimisation technique. As stated earlier, this could be compared with the experimental runs so that a juxtaposition of the two would lead to a better understanding of the system under differing conditions.

5. The condensed species that are likely to be present at equilibrium as per the formula (6.14) in the Cu segregation system for the input composition of the reactants considered in our study were Fe_3O_4 , FeO and Fe . These have to be incorporated and the analysis carried out. Inclusion of SiO_2 in the input ingredients would be ideal although the equilibrium solution to the problem would then be much more complex, due to the probability of the presence of a number of solid species.

6. A procedure similar to the one employed in the case of Copper may be tried for other potential metals amenable to Segregation Roasting like Antimony, Bismuth, Cobalt, Gold, Lead, Nickel, Palladium, Silver and Tin.

Appendix 3.1

The equilibrium constants of the various reactions are listed below

S.No.	Reactions	Equilibrium constants			
		1000°K	1100°K	1200°K	1300°K
1.	$\text{Cu}_2\text{O}(\text{s}) + 2\text{HCl}(\text{g}) = 2/3 \text{ Cu}_3\text{Cl}_3(\text{g}) + \text{H}_2\text{O}$	1.03×10^3	4.67×10^2	2.41×10^2	1.37×10^2
2.	$2/3 \text{ Cu}_3\text{Cl}_3(\text{g}) + \text{H}_2(\text{g}) = 2\text{Cu}(\text{s}) + 2\text{HCl}(\text{g})$	1.06×10^2	9.25×10	8.25×10	7.49×10
3.	$1/2 \text{ Fe}_2\text{SiO}_4(\text{s}) + 2\text{HCl}(\text{g}) = \text{FeCl}_2(\text{g})$ $+ 1/2 \text{ SiO}_2(\text{s}) + \text{H}_2\text{O}$	3.99×10^{-2}	8.77×10^{-2}	1.63×10^{-1}	2.67×10^{-1}
4.	$\text{Fe}_3\text{O}_4(\text{s}) + 6\text{HCl}(\text{g}) + \text{H}_2(\text{g}) = 3\text{FeCl}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$	1.72×10^{-2}	1.74×10^{-1}	1.07	4.53
5.	$\text{Fe}_2\text{O}_3(\text{s}) + 4\text{HCl}(\text{g}) + \text{H}_2(\text{g}) = 2\text{FeCl}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	1.85	8.72	2.95×10	7.80×10
6.	$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$	2.54	1.11×10	3.77×10	1.07×10^2
7.	$3\text{CuCl}(\text{g}) = \text{Cu}_3\text{Cl}_3(\text{g})$	8.62×10^{12}	3.43×10^{10}	3.50×10^8	7.37×10^6
8.	$\text{NiO}(\text{s}) + 2\text{HCl}(\text{g}) = \text{NiCl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	4.33×10^{-3}	1.60×10^{-2}	4.70×10^{-2}	1.16×10^{-1}
9.	$\text{NiCl}_2(\text{g}) + \text{H}_2(\text{g}) = \text{Ni}(\text{s}) + 2\text{HCl}(\text{g})$	5.56×10^4	1.48×10^4	4.96×10^3	2.38×10^3

APPENDIX 3,2

Equilibrium Log $P_{\text{CO}_2}/P_{\text{CO}}$ at different temperatures

Chemical species	1000°K	1100°K	1200°K	1300°K
1. $\text{Cu}_2\text{O}/\text{Cu}$	5.24	4.670	4.19	3.78
2. $\text{Fe}_2\text{SiO}_4/\text{Fe}_3\text{O}_4$	2.64	2.450	2.287	2.15
3. $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$	4.53	4.378	4.250	4.13
4. NiO/Ni	2.58	2.410	2.260	2.13

Appendix 6.1

Molal standard Free energy (in KCals/mole) of the
chemical species of interest at different temperatures (30)

Sl.No.	Chemical specie	F° at 800°K	F° at 900°K	F° at 1000°K	F° at 1100°K	F° at 1200°K	G° at 1300°K
1	2	3	4	5	6	7	8
1.	Cu(s)						
2.	Cu ₂ O(s)	-26.4	-24.76	-23.094	-21.456	-19.846	-18.265
3.	CuO(s)	-19.93	-17.909	-16.923	-13.97	-12.05	-10.161
4.	CuCl(g)	4.567	2.545	0.546	-1.428	-3.381	-5.313
5.	Cu ₃ Cl ₃ (g)	-60.848	-60.664	-60.462	-60.234	-59.986	-59.71
6.	Fe ₂ O ₃ (s)	-146.206	-140.248	-134.363	-128.461	-122.54	-116.616
7.	Fe ₃ O ₄ (s)	-203.874	-196.661	-189.541	-182.336	-175.096	-167.849
8.	FeO(s)	-52.427	-50.964	-49.495	-47.991	-46.479	-44.955
9.	Fe(s)	0.00	0.00	0.00	0.00	0.00	0.00
10.	FeCl(g)	37.765	35.154	32.602	30.134	27.725	25.365
11.	FeCl ₂ (g)	-42.73	-43.59	-44.43	-45.193	-45.912	-46.596
12.	FeCl ₃ (g)	-57.044	-56.532	-55.976	-55.348	-54.673	-53.960

1	2	3	4	5	6	7	8
13.	Fe ₂ Cl ₆ (g)	-121.791	-117.587	-113.341	-108.992	-104.583	-100.134
14.	H ₂ (g)	0.00	0.00	0.00	0.00	0.00	0.00
15.	H(g)	42.242	40.91	39.562	38.2	36.826	35.44
16.	HCl(g)	-23.774	-23.936	-24.093	-24.243	-24.39	-24.534
17.	H ₂ O(g)	-48.646	-47.352	-46.04	-44.712	-43.371	-42.022
18.	CO(g)	-43.612	-45.859	-47.859	-49.962	-52.049	-54.126
19.	CO ₂ (g)	-94.556	-94.596	-94.628	-94.658	-94.681	-94.70
20.	O ₂ (g)	0.0	0.0	0.0	0.0	0.0	0.0
21.	O(g)	47.96	46.422	44.875	43.318	41.755	40.186
22.	Cl ₂ (g)	0.0	0.0	0.0	0.0	0.0	0.0
23.	Cl(g)	18.347	16.952	15.547	14.133	12.713	11.286

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C... PROGRAM TO SOLVE A SET OF HIGHLY NONLINEAR EQUATIONS:
C... USING BROWN'S TECHNIQUE:

DIMENSION X(8),P(8),Q(8)

COMMON RR

COMMON C1,C2,C3

READ(20,*)C1,C2,C3

ITEMP=1200

WRITE(21,11)

WRITE(21,12),C1,C2,C3,ITEMP

WRITE(21,13)

WRITE(21,17)

WRITE(22,14);

WRITE(22,15),C1,C2,C3,ITEMP

WRITE(22,16)

11 FORMAT(2(/),T6,'REMARKS: Varying C')

12 format(2(/),T6,'WHEN C1=',F8.5,2X,'C2=',F8.5,2X,
1'C3=',F8.5,2X,'N1 SEGRN TEMP:=',I5)

13 FORMAT(T6,65(' '))

14 FORMAT(2(/),T16,'REMARKS: VARYING C2')

15 FORMAT(2(/),T16,'WHEN C1=',F8.5,2X,'C2=',F8.5,
12X,'C3=',F8.5,2X,'N1 SEGRN TEMP:=',I5)

16 FORMAT(T16,65(' '))

17 FORMAT(/,T16,'CO',T31,'CO2',T46,'H2',T61,'H2O',T76,
1'HCl',T91,'NiCl2',T106,'FeCl2',/)

DO 2 RR=0.0,4.0,0.25

OPEN(UNIT=35,DEVICE='DSK',FILE='FOR35.DAT')

READ(20,*) (X(I),I=1,8)

C TYPE*,X

DO 10 I=1,8

X(I)=ALOG10(X(I))

10 CONTINUE

C TYPE*,X

CALL NONLIN(8,8,100,1,X,1.0E-08)

C TYPE*,X

CALL EVAL(X,P,Q)

CLOSE(UNIT=35)

OPEN (UNIT=20,DEVICE='DSK',FILE='FOR20.DAT')

WRITE(20,*)X

CLOSE(UNIT=20)

2 CONTINUE

STOP

END

C N NUMBER OF EQUATIONS(=NO. OF UNKNOWNNS).

C SUMSIG NO. OF SIGNIFICANT DIGITS DESIRED.

C MAXIT MAXIMUM NO. OF ITERATIONS TO BE ALLOWED.

C IPRINT OUTPUT OPTION, OUTPUT IF = 1;

C X VECTOR OF INITIAL GUESSES.

C EPS CONVERGENCE CRITERION.

SUBROUTINE NONLIN(N,NUMSIG,MAXIT,IPRINT,X,EPS)

DIMENSION X(30),PART(30),TEMP(30),COE(30,31),ISUB(30)

DIMENSION LOOKUP(30,30),GNDRE(5)

```

04400
04500 C      DELTA WILL BE A FUNCTION OF THE MACHINE AND THE PRECISION USED
04600
04700      DELTA=1.E-07
04800      RELCON=10.0E+0**(-NUMSIG)
04900      JTEST=1
05000      IF(IPRINT.EQ.1) WRITE(35,48)
05100 48      FORMAT(1H1)
05200      DO 700 M=1,MAXIT
05300      IQUIT=0
05400      FMAX=0.
05500      M1=M-1
05600      IF(IPRINT.NE.1) GO TO 9
05700      WRITE(35,49) M1,(X(I),I=1,N)
05800 49      FORMAT(/T41,I5/(T41,6E18.8))
05900 9      DO 10 J=1,N
06000 10      LOOKUP(1,J)=J
06100
06200 C      THE ARRAY LOOKUP PERMITS A PARTIAL PIVOTING EFFECT WITHOUT
06300 C      HAVING TO PHYSICALLY INTERCHANGE ROWS OR COLUMNS.
06400
06500      DO 500 K=1,N
06600      IF(K-1) 134,134,131
06700 131      KMIN=K-1
06800      CALL BACK(KMIN,N,X,ISUB,COE,LOOKUP)
06900
07000 C      SET UP PARTIAL DERIVATIVES OF KTH FUNCTION.
07100
07200 134      CALL AUXFUN(X,F,K)
07300      FMAX=AMAX1(FMAX,ABS(F))
07400      IF(ABS(F).GE.EPS) GO TO 1345
07500      IQUIT=IQUIT+1
07600      IF(IQUIT.NE.N) GO TO 1345
07700      GO TO 725
07800 1345      FACTOR=0.001E+00
07900 135      ITALLY=0
08000      DO 200 I=K,N
08100      ITEMP=LOOKUP(K,I)
08200      HOLD=X(ITEMP)
08300      PREC=5.0E-6
08400
08500 C      PREC IS A FUNCTION OF THE MACHINE SIGNIFICANCE, SIG, AND SHOULD
08600 C      BE COMPUTED AS PREC=5.*10.**(-SIG+2). IN THIS INSTANCE WE WERE
08700 C      DEALING WITH AN 8 DIGIT MACHINE.
08800
08900      ETA=FACTOR*ABS(HOLD)
09000      H=AMIN1(FMAX,ETA)
09100      IF(H.LT.PREC) H=PREC
09200      X(ITEMP)=HOLD+H
09300      IF(K-1) 161,161,151
09400 151      CALL BACK(KMIN,N,X,ISUB,COE,LOOKUP)
09500 161      CALL AUXFUN(X,FPLUS,K)
09600      PART(ITEMP)=(FPLUS-F)/H
09700      X(ITEMP)=HOLD
09800      IF(ABS(PART(ITEMP)).LT.DELTA) GO TO 190
09900      IF(ABS(F/PART(ITEMP)).LE.1.0E+15) GO TO 200
10000 190      ITALLY=ITALLY+1
10100 200      CONTINUE
10200      IF(ITALLY.LE.N-K) GO TO 202
10300      FACTOR=FACTOR*10.0E+00
10400      IF(FACTOR.GT.11.) GO TO 775

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10500
10600 202 GO TO 135
10700 IF(K.LT.N) GO TO 203
10800 IF( ABS(PART(ITEMP)).LT.DELTA ) GO TO 775
10900 COE(K,N+1)=0.0E+00
11000 KMAX=ITEMP
11100 GO TO 500
11200
11300 C FIND PARTIAL DERIVATIVE OF LARGEST ABSOLUTE VALUE
11400
11500 203 KMAX=LOOKUP(K,K)
11600 DERMAT=ABS(PART(KMAX))
11700 KPLUS=K+1
11800 DO 210 I=KPLUS,N
11900 JSUB=LOOKUP(K,I)
12000 TEST=ABS(PART(JSUB))
12100 IF(TEST.LT.DERMAT) GO TO 209
12200 DERMAT=TEST
12300 LOOKUP(KPLUS,I)=KMAX
12400 KMAX=JSUB
12500 GO TO 210
12600 209 LOOKUP(KPLUS,I)=JSUB
12700 210 CONTINUE
12800 IF( ABS(PART(KMAX)).EQ.0.0) GO TO 775
12900
13000 C SET UP COEFFICIENTS FOR KTH ROW OF TRIANGULAR LINEAR SYSTEM USE
13100 C TO BACK - SOLVE FOR THE FIRST K VALUES OF X(I)
13200 ISUB(K)=KMAX
13300 COE(K,N+1)=0.0E+00
13400 DO 220 J=KPLUS,N
13500 JSUB=LOOKUP(KPLUS,J)
13600 COE(K,JSUB)=-PART(JSUB)/PART(KMAX)
13700 COE(K,N+1)=COE(K,N+1)+PART(JSUB)*X(JSUB)
13800 220 CONTINUE
13900 500 COE(K,N+1)=(COE(K,N+1)-F)/PART(KMAX)+X(KMAX)
14000
14100 C BACK SUBSTITUTE TO OBTAIN NEXT APPROXIMATION TO X
14200
14300 X(KMAX)=COE(N,N+1)
14400 IF(N.EQ.1) GO TO 610
14500 CALL BACK(N-1,N,X,ISUB,COE,LOOKUP)
14600 610 IF(M-1) 650,650,625
14700
14800 C TEST FOR CONVERGENCE
14900
15000 625 DO 630 I=1,N
15100 IF( ABS(TEMP(I)-X(I)).GT.ABS(X(I))*RELCON ) GO TO 649
15200 630 CONTINUE
15300 JTEST=JTEST+1
15400 IF(JTEST-3) 650,725,725
15500 649 JTEST=1
15600 650 DO 660 I=1,N
15700 660 TEMP(I)=X(I)
15800 700 CONTINUE
15900 WRITE(35,1753)
16000 1753 FORMAT(/T41,'NO CONVERGENCE. MAXIMUM NUMBER OF ITERATIONS USED')
16100 IF(IPRINT.NE.1) GO TO 800
16200 WRITE(35,1763)
16300 1763 FORMAT(/T41,'FUNCTION VALUES AT THE LAST APPROXIMATION FOLLOW')
16400 IFLAG=1
16500 GO TO 777

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16600 725 IF(IPRINT.NE.1) GO TO 800
16700 7777 DO 750 K=1,N
16800 CALL AUXFUN(X,PART(K),K)
16900 750 CONTINUE
17000 IF(IFLAG.NE.1) GO TO 8777
17100 WRITE(35,7788) (PART(K),K=1,N)
17200 7788 FORMAT((T41,6E20.8))
17300 GO TO 800
17400 8777 WRITE(35,751)
17500 751 FORMAT(/T41,'CONVERGENCE HAS BEEN ACHIEVED. THE FUNCTION VALUES
17600 WRITE(35,7515) (PART(K),K=1,N)
17700 7515 FORMAT(T41,'AT THE FINAL APPROXIMATION FOLLOW:')(T41,6E20.8))
17800 GO TO 800
17900 775 WRITE(35,752)
18000 752 FORMAT(/T41,'MODIFIED JACOBIAN IS SINGULAR. TRY A DIFFERENT')
18100 WRITE(35,7525)
18200 7525 FORMAT(T41,'INITIAL APPROXIMATION.')
18300 900 MAXIT=M1+1
18400 RETURN
18500 END

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```

19000 C SUBROUTINE BACK(KMIN,N,X,ISUB,COE,LOOKUP)
19100 C THIS SUBROUTINE BACK-SOLVES THE FIRST KMIN ROWS OF A TRIANGULAR
19200 C LINEAR SYSTEM FOR IMPROVED X VALUES IN TERMS PREVIOUS ONES.
19300 DIMENSION X(30),COE(30,31),ISUB(30),LOOKUP(30,30)
19400 DO 200 KK=1,KMIN
19500 KM=KMIN-KK+2
19600 KMAX=ISUB(KM-1)
19700 X(KMAX)=0.0E+00
19800 DO 100 J=KM,N
19900 JSUB=LOOKUP(KM,J)
20000 X(KMAX)=X(KMAX)+COE(KM-1,JSUB)*X(JSUB)
20100 100 CONTINUE
20200 X(KMAX)=X(KMAX)+COE(KM-1,N+1)
20300 200 CONTINUE
20400 RETURN
20500 END

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```

20600 SUBROUTINE AUXFUN(X,Y,K)
20700 DIMENSION X(8)
20800 COMMON RR
20900 COMMON C1,C2,C3
20950
21000 C data a11,AL2/2.13,2.15/
21100
21125 C DATA AL1,AL2/2.26,2.287/
21137 C DATA AL1,AL2/2.41,2.45/
21150 C
21200 C AK1=.116; AK2=2.38E3; AK3=4.53;
21250 C AK4=.267; AK5=.594
21262 C AK1=1.6E-02; AK2=1.48E4; AK3=.174;
21268 C AK4=0.0877; AK5=1.09
21271 C AK1=4.7E-2; AK2=4.96E3; AK3=1.07;
21273 AK4=0.163; AK5=0.783
21275
21300 GK2=ALOG10(AK2); GK4=ALOG10(AK4)
21500 GK1=ALOG10(AK1); GK3=ALOG10(AK3)
21600 GK5=ALOG10(AK5);
21700

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21800      GO TO (1,2,3,4,5,6,7,8),K
21900
22000      1      Y=(C1-(10.*X(1)+10.*X(2)))
22100      RETURN
22200
22300      2      Y=(C2-(10.*X(4)+10.*X(3)+0.5*10.*X(5)))
22400      RETURN
22500
22600      3      Y=(C3-(0.5*10.*X(5)+10.*X(7)+10.*X(6)))
22700      RETURN
22800
22900      4      Y=((10.*X(8))-(10.*X(1)+10.*X(2)+10.*X(3)+10.*X(4)
23000      1+10.*X(5)+10.*X(6)+10.*X(7)))
23100      RETURN
23200
23300      5      Y=(RR-(X(2)-X(1)))
23400      RETURN
23500
23600      6      Y=(GK5-(X(2)+X(3)-X(1)-X(4)))
23700      RETURN
23800
23850      7      IF(RR.GE.AL1) GO TO 10
23900      Y=(GK2-(2.*X(5)-X(6)-X(3)))
23950      GO TO 31
23990      10      Y=(GK1-(X(6)+X(4)-2.*X(5)))
23995      31      RETURN
24100
24112      8      IF (RR.LT.AL2)GO TO 73
24123      Y=(GK3-(3.*X(7)+4.*X(4)-6.*X(5)-X(3)))
24125      GO TO 77
24150      73      Y=(GK4-(X(7)+X(4)-2.*X(5)))
24162      77      RETURN
25000      END
25100
25200      SUBROUTINE EVAL(X,P,O)
25300      C..      THIS SUBROUTINE EVALUATES EQBM & STOICH CONST
25400      DIMENSION X(8),P(8),Q(8)
25500      COMMON RR
25600      DO 22 I=1,8
25700      X(I)=10.*X(I)
25800      22      CONTINUE
25900
26000      DO 11 I=1,7
26100      P(I)=X(I)/X(8)
26200      Q(I)=ALOG10(P(I))
26300      11      CONTINUE
26400
26500      WRITE(21,1)RR,(Q(I),I=1,7)
26600      WRITE(22,2)RR,(X(I),I=1,4)
26700      WRITE(22,3)(X(I),I=5,8)
26800      WRITE(22,4)(P(I),I=1,4)
26900      WRITE(22,5)(P(I),I=5,7)
27000      RETURN
27100      1      FORMAT(/,T6,F4.2,7F15.6)
27200      2      FORMAT(/,T16,F4.2,T20,4E20.8)
27300      3      FORMAT(T20,4E20.8)
27400      4      FORMAT(/,T20,4E20.8)
27500      5      FORMAT(T20,3E20.8)
27600      END

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00001 C      PROGRAM FOR THE SOLUTION OF A SYSTEM OF NONLINEAR
00011 C..    SIMULTANEOUS ALGEBRAIC EQUATIONS BY THE HYBRID
00021 C..    METHOD DUE TO POWELL
00031
00041 C..    C1,C2,C3 : STOICHIOMETRIC VALUES
00051 C..    RA: LOG P'CO2/P'CO
00100 C..    DIMENSION X(9),F(9),AJINV(9,9),W(250)
00101 COMMON RA
00141 DATA C1,C2,C3/0.025,0.0633,0.0154/
00181 N=9; MAXFUN=900; ACC=1.E-08
00221 STEP=SQRT(FTOL)
00261 DMAX=5.0
00381
00421 OPEN(UNIT=30,DEVICE='DSK',FILE='E.CDR')
00431 C..    FEED THE FLAT START VALUES
00441 C..    AND THE RATIO OF LOG P'CO2/P'CO
00461 READ(30,*) (X(I),I=1,8)
00501 READ(30,*) RA
00511 C..    X(9) IS TOTAL NO OF MOLES
00541 X(9)=0.
00581 DO 5 I=1,8
00621 X(9)=X(9)+X(I)
00661 5 CONTINUE
00671
00701 DO 10 I=1,9
00741 X(I)=ALOG10(X(I))
00781 10 CONTINUE
00821
00900 CALL NONLIN(2,X,F,AJINV,STEP,DMAX,ACC,MAXFUN,1,W)
00910 CALL EVAL(X,P,Q)
00920 CLOSE(UNIT=30)
01000 CALL EXIT
01100 END
01200
01300 SUBROUTINE CALFUN(N,X,F)
01400 DIMENSION X(9),F(9)
01401 DIMENSION X(9),RC(9)
01403 COMMON RA
01404 C..    AL'S REPRESENT STABILITY BOUNDARIES
01405 C..    DATA C1,C2,C3/0.0307,0.0711,0.0154/
01407 DATA C1,C2,C3/0.025,0.0633,0.0154/
01409 C..    DATA AL1,AL2,AL3/4.67,2.45,4.38/
01411
01412 C..    AK'S REPRESENT EQBM CONSTANTS
01413 AK2=92.5; AK4=.174; AK6=1.09; AK7=3.43E+10
01415 AK1=467.; AK3=8.72; AK5=.0877
01417 GK2=ALOG10(AK2); GK4=ALOG10(AK4)
01419 GK6=ALOG10(AK6); GK7=ALOG10(AK7)
01421 GK1=ALOG10(AK1); GK3=ALOG10(AK3)
01423 GK5=ALOG10(AK5);
01425
01429 C..    F'S REPRESENT THE FUNCTIONS WHOSE ZERO'S ARE REQD
01430 F(1)=C1-(10.*X(1))+10.*X(2))
01431
01433 F(2)=C2-(10.*X(3)+10.*X(4)+0.5*10.*X(5))
01435
01437 F(3)=C3-(10.*X(5)+2.0*10.*X(8)+3.0*10.*X(7)+10.*X(6))
01439
01441 F(4)=(10.*X(9))-(10.*X(1)+10.*X(2)+10.*X(3)+10.*X(4)
01443 1+10.*X(5)+10.*X(6)+10.*X(7)+10.*X(8))
01445

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01447
01449 F(5)=RA-(X(2)-X(1))
01451
01453 F(6)=GK2-(2.*X(5)-(2./3.)*X(7)-X(3)-(1./3.)*X(9))
01455 C F(6)=GK1-((2./3.)*X(7)+X(4)+(1./3.)*X(9)-2.*X(5))
01457
01459 C F(7)=GK4-(3.*X(8)+4.*X(4)-6.*X(5)-X(3))
01461 F(7)=GK5-(X(8)+X(4)-2.*X(5))
01463 C F(7)=GK3-(2.*X(8)+3.*X(4)-4.*X(5)-X(3))
01465
01467 F(8)=GK6-(X(2)+X(3)-X(1)-X(4))
01469
01471 F(9)=GK7-(X(7)+2.*X(9)-3.*X(6))
01473 RETURN
01475 END
01477
01479 SUBROUTINE EVAL(X,P,Q)
01480 C.. THIS SUBROUTINE CALCULATES THE EQBM AND STOICHIOMY VALUES
01481
01483 DIMENSION X(9),P(9),Q(9)
01485 COMMON RA
01487 C DATA AL1,AL2,AL3/4.67,2.45,4.378/
01489 ITEMP=1100
01491 DO 22 I=1,9
01493 X(I)=10.^X(I)
01495 22 CONTINUE
01497
01499 DO 11 I=1,8
01501 P(I)=X(I)/X(9)
01503 Q(I)=ALOG10(P(I))
01505 11 CONTINUE
01507
01509 WRITE(20,7)
01511 WRITE(20,8)
01513 WRITE(20,4),X(1),P(1),Q(1)
01515 WRITE(20,5),X(2),P(2),Q(2)
01517 WRITE(20,6),X(3),P(3),Q(3)
01519 WRITE(20,15),X(4),P(4),Q(4)
01521 WRITE(20,2),X(5),P(5),Q(5)
01523 WRITE(20,35),X(6),P(6),Q(6)
01525 WRITE(20,3),X(7),P(7),Q(7)
01527 WRITE(20,25),X(8),P(8),Q(8)
01529
01531 C IF (RR.GE.AL1)GO TO 71
01533 F2=X(5)^2/(X(7)^(2./3.)*X(3)*X(9)^(1./3.))
01535 TYPE*,F2
01537 WRITE(20,55),F2
01541
01543 C F1=(X(7)^(2./3.)*X(4)*X(9)^(1./3.))/X(5)^2
01545 CC TYPE *,F1
01547 C WRITE(20,53),F1
01551
01553 C IF (RR.LT.AL2)GO TO 73
01555 C IF (RR.GE.AL3)GO TO 74
01557
01559 C F4=(X(8)^3*X(4)^4)/(X(5)^6*X(3))
01561 CC TYPE*,F4
01563 CC WRITE(20,65),F4
01565 C GO TO 77
01567
01571 F5=X(8)*X(4)/(X(5)^2)

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01573 TYPE*,F5
01575 WRITE(20,61),F5
01579
01583 C F3=(X(8)^2*X(4)^3)/(X(5)^4*X(3))
01585 C TYPE*,F3
01587 C WRITE(20,62),F3
01591
01593 F6=(X(2)*X(3))/(X(1)*X(4))
01595 TYPE*,F6
01597 WRITE(20,75),F6
01599
01601 F9=(X(7)*X(9)^2)/X(6)^3
01603 TYPE*,F9
01605 WRITE(20,90),F9
01607
01609 F7=X(2)/X(1)
01611 WRITE(20,85),F7
01613 TYPE*,F7
01615
01617 CC1=X(1)+X(2)
01619 WRITE(20,86),CC1
01621
01623 CC2=X(3)+X(4)+0.5*X(5)
01625 WRITE(20,87),CC2
01627
01629 CC3=X(5)+2.*X(8)+3.*X(7)+X(6)
01631 WRITE(20,88),CC3
01633
01635 WRITE(20,45),X(9)
01637 WRITE(20,46),RA
01639 WRITE(20,13),ITEMP
01641
01643 RETURN
01645 90 FORMAT(/,25X,'MONO-TRIMER EOM CONSTANT=',1PE20.8)
01647 88 FORMAT(/,25X,'SUM FROM C1 BALANCE=',F13.8)
01649 87 FORMAT(/,25X,'SUM FROM H2 BALANCE=',F13.8)
01651 86 FORMAT(/,25X,'SUM FROM C BALANCE=',F14.8)
01653 85 FORMAT(/,25X,'P CO2/P CO RATIO=',F13.5)
01655 75 FORMAT(/,25X,'CO-H2O/CO2-H2 EQBM CONSTANT=',F13.8)
01657 55 FORMAT(/,25X,'Cu3C13 REDN EOM CONST=',F15.8)
01659 53 FORMAT(/,25X,'CU OXIDE CHLN EQ CONS=',F14.8)
01661 65 FORMAT(/,25X,'MAGNETITE CHLN EQ CONS=',F14.8)
01663 61 FORMAT(/,25X,'SILICATE CHLN EQ CONS=',F14.8)
01665 62 FORMAT(/,25X,'HAMETITE CHLN EQ CONS=',F14.8)
01667 45 FORMAT(/,25X,'TOTAL MOLES(CALC)=',E19.8)
01669 46 FORMAT(/,25X,'LOG P CO2/P CO RAT=',F8.3)
01671 13 FORMAT(/,25X,'SEGREGN TEMPERATURE=',I7,'K.')
01673 7 FORMAT(10(/,T42,'No OF MOLES',T66,'P PRESSURES',T90,'LOG P PR
01675 8 FORMAT(T42,'-----',T66,'-----',T90,'-----')
01677 35 FORMAT(/,25X,'CuCl',T41,E15.8,T65,E15.8,T90,F11.8)
01679 25 FORMAT(/,25X,'FeCl2',T41,E15.8,T65,E15.8,T90,F11.8)
01681 15 FORMAT(/,25X,'H2O',T41,E15.8,T65,E15.8,T90,F11.8)
01683 2 FORMAT(/,25X,'HCL',T41,E15.8,T65,E15.8,T90,F11.8)
01685 3 FORMAT(/,25X,'Cu3C13',T41,E15.8,T65,E15.8,T90,F11.8)
01687 4 FORMAT(/,25X,'CO',T41,E15.8,T65,E15.8,T90,F11.8)
01689 5 FORMAT(/,25X,'CO2',T41,E15.8,T65,E15.8,T90,F11.8)
01691 6 FORMAT(/,25X,'H2',T41,E15.8,T65,E15.8,T90,F11.8)
01693 CLOSE(UNIT=19)
01695 END
01697
01900

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02000 SUBROUTINE NONLIN(N,X,F,AJINV,DSTEP,DMAX,ACC,MAXFUN,IPRINT,W)
02100 DIMENSION X(9),F(9),AJINV(N,N),W(9)
02200 C SET VARIOUS PARAMETERS
02300 MAXC = 0
02400 C 'MAXC' COUNTS THE NUMBER OF CALLS OF CALFUN
02500 NT = N+4
02600 NTEST = NT
02700 C 'NT' AND 'NTEST' CAUSE AN ERROR RETURN IF F(X) DOES NOT DECREASE
02800 DTEST = FLOAT(N+N)-0.5
02900 C 'DTEST' IS USED TO MAINTAIN LINEAR INDEPENDENCE
03000 NX = N*N
03100 NF = NX+N
03200 NW = NF+N
03300 MW = NW+N
03400 NDC = MW+N
03500 ND = NDC+N
03600 C THESE PARAMETERS SEPARATE THE WORKING SPACE ARRAY W
03700 FMIN = 0
03800 C USUALLY 'FMIN' IS THE LEAST CALCULATED VALUE OF F(X),
03900 C AND THE BEST X IS IN W(NX+1) TO W(NX+N)
04000 DD = 0.
04100 C USUALLY 'DD' IS THE SQUARE OF THE CURRENT STEP LENGTH
04200 DSS = DSTEP*DSTEP
04300 DM = DMAX*DMAX
04400 DMM = 4.*DM
04500 IS = 5
04600 C 'IS' CONTROLS A 'GOTO' STATEMENT FOLLOWING A CALL OF CALFUN
04700 TINC = 1.
04800 C 'TINC' IS USED IN THE CRITERION TO INCREASE THE STEP LENGTH
05000 IF (IPRINT) 1,1,85
05100 85 PRINT 86
05200 86 FORMAT(1H1)
05300 C CALL THE SUBROUTINE CALFUN
05400 1 MAXC = MAXC+1
05500 CALL CALFUN(N,X,F)
05600 C TEST FOR CONVERGENCE
05700 FSQ = 0
05800 DO 2 I=1,N
05900 FSQ = FSQ+F(I)*F(I)
06000 2 CONTINUE
06100 IF (FSQ-ACC) 3,3,4
06200 C 3 PROVIDE PRINTING OF FINAL SOLUTION IF REQUESTED
06300 3 IF (IPRINT) 5,5,6
06400 6 PRINT 7,MAXC
06500 7 FORMAT(///5X,'THE FINAL SOLUTION CALCULATED BY NONLIN REQUIRED'
06600 1,15,'CALLS OF CALFUN, IS')
06700 PRINT 8,(I,X(I),F(I),I=1,N)
06800 8 FORMAT(//4X,'I',7X,'X(I)',12X,'F(I)')/(15,2E17.8))
06900 PRINT 9,FSQ
07000 9 FORMAT(/5X,'THE SUM OF SQUARES IS',E17.8)
07100 5 RETURN
07200 C TEST FOR ERROR RETURN BECAUSE F(X) DOES NOT DECREASE
07300 4 GO TO (10,11,11,10,11),IS
07400 10 IF (FSQ-FMIN) 15,20,20
07500 20 IF (DD-DSS) 12,12,11
07600 12 NTEST = NTEST-1
07700 IF (NTEST) 13,14,11
07800 14 PRINT 16,NT
07900 16 FORMAT(///5X,'ERROR RETURN FROM NONLIN BECAUSE',15,
08000 1,'CALLS OF CALFUN FAILED TO IMPROVE THE RESIDUALS')
08100 17 DO 18 I=1,N

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```

08200      X(I) = W(NX+I)
08300      F(I) = W(NF+I)
08400      18      CONTINUE
08500      FSO = FMIN
08600      GOTO 3
08700      C      ERROR RETURN BECAUSE A NEW JACOBIAN IS UNSUCCESSFUL
08800      13      PRINT 19
08900      19      FORMAT(///5X,'ERROR RETURN FROM NONLIN BECAUSE F(X)',
09000      1'FAILED TO DECREASE USING A NEW JACOBIAN')
09100      GOTO 17
09200      15      NTEST = NT
09300      C      TEST WHETHER THERE HAVE BEEN MAXFUN CALLS OF CALFUN
09400      11      IF (MAXFUN-MAXC) 21,21,22
09500      21      PRINT 23,MAXC
09600      23      FORMAT(///5X,'ERROR RETURN FROM NONLIN BECAUSE THERE HAVE BEEN',
09700      1 15,'CALLS OF CALFUN')
09800      IF (FSQ-FMIN) 3,17,17
09900      C      PROVIDE PRINTING IF REQUESTED
10000      22      IF (IPRINT) 24,24,25
10100      25      PRINT 26,MAXC
10200      26      FORMAT(///5X,'AT THE',I5,'TH CALL OF CALFUN WE HAVE')
10300      PRINT 8,(I,X(I),F(I),I=1,N)
10400      PRINT 9,FSQ
10500      24      GOTO (27,28,29,87,30),IS
10600      C      STORE THE RESULT OF THE INITIAL CALL OF CALFUN
10700      30      FMIN = FSO
10800      DO 31 I=1,N
10900      W(NX+I) = X(I)
11000      W(NF+I) = F(I)
11100      CONTINUE
11200      C      CALCULATE A NEW JACOBIAN APPROXIMATION
11300      32      IC = 0
11400      IS = 3
11500      33      IC = IC+1
11600      X(IC) = X(IC)+DSTEP
11700      GOTO 1
11800      29      K = IC
11900      DO 34 I=1,N
12000      W(K) = (F(I)-W(NF+1))/DSTEP
12100      K = K+N
12200      34      CONTINUE
12300      X(IC) = W(NX+IC)
12400      IF (IC-N) 33,35,35
12500      C      CALCULATE THE INVERSE OF THE JACOBIAN AND SET THE DIRECTION
12600      35      MATRIX
12700      K = 0
12800      DO 36 I=1,N
12900      DO 37 J=1,N
13000      K = K+1
13100      AJINV(I,J) = W(K)
13200      W(ND+K) = 0.
13300      37      CONTINUE
13400      W(NDC+K+I) = 1
13500      W(NDC+I) = 1.+FLOAT(N-I)
13600      36      CONTINUE
13700      CALL MB01B(AJINV,N,N)
13800      C      START ITERATION BY PRIDICTING THE DESCENT & NEWTON MINIMA
13900      38      DS = 0.
14000      DN = 0.
14100      SP = 0.
14200      DO 39 I=1,N

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14300 X(J) = 0.
14400 F(I) = 0.
14500 K = I
14600 DO 40 J=1,N
14700 X(I) = X(I)-W(K)*W(NF+J)
14800 F(I) = F(I)-AJINV(I,J)*W(NF+J)
14900 K = K+N
15000 40 CONTINUE
15100 DS = DS+X(I)*X(I)
15200 DN = DN+F(I)*F(I)
15300 SP = SP+X(I)*F(I)
15400 39 CONTINUE
15500 C TEST WHETHER A NEARBY STATIONARY POINT IS PRIDICTED
15600 IF (FMIN*FMIN-DS) 41,41,42
15700 C IF SO THEN RETURN OR REVISE JACOBIAN
15800 42 GOTO (43,43,44),IS
15900 44 PRINT 45
16000 45 FORMAT(/'5X, 'ERRORRETURN FROM NONLIN BECAUSE A NEARBY',
16100 1 'STATIONARY POINT OF F(X) IS PREDICTED')
16200 GOTO 17
16300 43 NTEST = 0
16400 DO 46 I=1,N
16500 X(I) = W(NX+I)
16600 46 CONTINUE
16700 GOTO 32
16800 C TEST WHETHER TO APPLY THE FULL NEWTON CORRECTION
16900 41 IS = 2
17000 IF (DN-DD) 47,47,48
17100 47 DD = AMAX1(DN,DSS)
17200 DS = 0.25*DN
17300 TINC = 1.
17400 IF (DN-DSS) 49,58,58
17500 49 IS = 4
17600 GOTO 80
17700 C CALCULATE THE LENGTH OF TTHE STEEPEST DESCENT STEP
17800 48 K = 0
17900 DMULT = 0.
18000 DO 51 I=1,N
18100 DW = 0.
18200 DO 52 J=1,N
18300 K = K+1
18400 DW = DW+W(K)*X(J)
18500 52 CONTINUE
18600 DMULT = DMULT+DW*DW
18700 51 CONTINUE
18800 DMULT = DS/DMULT
18900 DS = DS*DMULT*DMULT
19000 C TEST WHETHER TO USE THE STEEPEST DESCENT DIRECTION
19100 IF (DS-DD) 53,54,54
19200 C TEST WHETHER THE INITIAL VALUEOF DD HAS BEEN SET
19300 54 IF (DD) 55,55,56
19400 55 DD = AMAX1(DSS,AMIN1(DM,DS))
19500 DS = DS/(DMULT*DMULT)
19600 GOTO 41
19700 C SET THE MULTIPLIER OF THE STEEPEST DESCENT DIRECTION
19800 56 ANMULT = 0.
19900 DMULT = DMULT*SQRT(DD/DS)
20000 GOTO 98
20100 C INTERPOLATE BETWEEN THE STEEPEST DESCENT & THE NEWTON DIRECTIONS
20200 53 SP = SP*DMULT
20300 ANMULT = (DD-DS)/((SP-DS)+SQRT((SP-DD)**2+(DN-DD)*(DD-DS)))

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20400      DMULT = DMULT*(1.-ANMULT)
20500      CALCULATE THE CHANGE IN X AND ITS ANGLE WITH THE FIRST DIRECTION
C 98      DN = 0.
20600      SP = 0.
20700      DO 57 I=1,N
20800      F(I) = DMULT*X(I)+ANMULT*F(I)
20900      DN = DN+F(I)*F(I)
21000      SP = SP+F(I)*W(ND+I)
21100      57 CONTINUE
21200      DS = 0.25*DN
21300      C TEST WHETHER AN EXTRA STEP IS NEEDED FOR INDEPENDENCE
21400      IF (W(NDC+1)-DTEST) 58,58,59
21500      59 IF (SP*SP-DS) 60,58,58
21600      C TAKE THE EXTRA STEP & UPDATE THE DIRECTION MATRIX
21700      50 IS = 2
21800      60 DO 61 I=1,N
21900      X(I) = W(NX+I)+DSTEP*W(ND+I)
22000      W(NDC+I) = W(NDC+I+1)+1.
22100      61 CONTINUE
22200      W(ND) = 1.
22300      DO 62 I=1,N
22400      K = ND+I
22500      SP = W(K)
22600      DO 63 J=2,N
22700      W(K) = W(K+N)
22800      K = K+N
22900      63 CONTINUE
23000      W(K) = SP
23100      62 CONTINUE
23200      GOTO 1
23300      C EXPRESS THE NEW DIRECTION IN TERMS OF THOSE OF THE DIRECTION
23400      C MATRIX, AND UPDATE THE COUNTS IN W(NDC+1) ETC.
23500      58 SP = 0.
23600      K = ND
23700      DO 64 I=1,N
23800      X(I) = DW
23900      DW = 0.
24000      DO 65 J=1,N
24100      K = K+1
24200      DW = DW+F(J)*W(K)
24300      65 CONTINUE
24400      GOTO (68,66), IS
24500      66 W(NDC+I) = W(NDC+I)+1.
24600      SP = SP+DW*DW
24700      IF (SP-DS) 64,64,67
24800      67 IS = 1
24900      KK = I
25000      X(1) = DW
25100      GOTO 69
25200      68 X(I) = DW
25300      69 W(NDC+I) = W(NDC+I+1)+1.
25400      64 CONTINUE
25500      W(ND) = 1.
25600      C REORDER THE DIRECTIONS SO THAT KK IS FIRST
25700      IF (KK-1) 70,70,71
25800      71 KS = NDC+KK*N
25900      DO 72 I=1,N
26000      KS = KS+1
26100      SP = W(K)
26200      DO 73 J=2,KS
26300      W(K) = W(K-N)
26400

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26500      K = K-N
26600      73      CONTINUE
26700      W(K) = SP
26800      72      CONTINUE
26900      C      GENERATE THE NEW ORTHOGONAL DIRECTION MATRIX
27000      70      DO 74 I=1,N
27100      W(NW+I) = 0.
27200      74      CONTINUE
27300      SP = X(1)*X(1)
27400      K = ND
27500      DO 75 I=2,N
27600      DS = SORT(SP*(SP+X(I)*X(I)))
27700      DW = SP/DS
27800      DS = X(I)/DS
27900      SP = SP+X(I)*X(I)
28000      DO 76 J=1,N
28100      K = K+1
28200      W(NW+J) = W(NW+J)+X(I-1)*W(K)
28300      W(K) = DW*W(K+N)-DS*W(NW+J)
28400      76      CONTINUE
28500      75      CONTINUE
28600      SP = 1./SORT(DN)
28700      DO 77 I=1,N
28800      K = K+1
28900      W(K) = SP*F(I)
29000      77      CONTINUE
29100      C      CALCULATE THE NEXT VECTOR X, AND PREDICT THE RIGHT HAND SIDES
29200      80      FNP = 0.
29300      K = 0
29400      DO 78 I=1,N
29500      X(I) = W(NX+I)+F(I)
29600      W(NW+I) = W(NF+I)
29700      DO 79 J=1,N
29800      K = K+1
29900      W(NW+I) = W(NW+I)+W(K)*F(J)
30000      79      CONTINUE
30100      FNP = FNP+W(NW+I)**2
30200      78      CONTINUE
30300      C      CALL CALFUN USING THE NEW VECTOR OF VARIABLES
30400      GOTO 1
30500      C      UPDATE THE STEP SIZE
30600      27      DMULT = 0.9*FMIN+0.1*FNP-FSQ
30700      IF(DMULT) 82,81,81
30800      82      DD = AMAX1(DSS,0.25*DD)
30900      TINC = 1.
31000      IF (FSQ-FMIN) 83,28,28
31100      C      TRY THE TEST TO DECIDE WHETHER TO INCREASE THE STEP LENGTH
31200      81      SP = 0.
31300      SS = 0.
31400      DO 84 I=1,N
31500      SP = SP+ABS(F(I)*(F(I)-W(NW+I)))
31600      SS = SS+(F(I)-W(NW+I))**2
31700      84      CONTINUE
31800      PJ = 1.+DMULT/(SP+SORT(SP*SP+DMULT*SS))
31900      SP = AMIN1(4.,TINC,PJ)
32000      TINC = PJ/SP
32100      DD = AMIN1(DM,SP*DD)
32200      GOTO 83
32300      C      IF F(X) IMPROVES STORE THE NEW VALUE OF X
32400      87      IF (FSQ-FMIN) 83,50,50
32500      83      FMIN = FSQ

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32600 DO 88 I=1,N
32700 SP = X(I)
32800 X(I) = W(NX+I)
32900 W(NX+I) = SP
33000 SP = F(I)
33100 F(I) = W(NF+I)
33200 W(NF+I) = SP
33300 W(NW+I) = -W(NW+I)
33400 88 CONTINUE
33500 IF (IS-1) 28,28,50
33600 C CALCULATE THE CHANGES IN F AND IN X
33700 28 DO 89 I=1,N
33800 X(I) = X(I)-W(NX+I)
33900 F(I) = F(I)-W(NF+I)
34000 89 CONTINUE
34100 C UPDATE THE APPROXIMATIONS TO J AND TO AJINV
34200 K = 0
34300 DO 90 I=1,N
34400 W(MW+I) = X(I)
34500 W(NW+I) = F(I)
34600 DO 91 J=1,N
34700 W(MW+I) = W(MW+I)-AJINV(I,J)*F(J)
34800 K = K+1
34900 W(NW+I) = W(NW+I)-W(K)*X(J)
35000 91 CONTINUE
35100 90 CONTINUE
35200 SP = 0.
35300 SS = 0.
35400 DO 92 I=1,N
35500 DS = 0.
35600 DO 93 J=1,N
35700 DS = DS+AJINV(J,I)*X(J)
35800 93 CONTINUE
35900 SP = SP+DS*F(I)
36000 SS = SS+X(I)*X(I)
36100 F(I) = DS
36200 92 CONTINUE
36300 DMULT = 1.
36400 IF (ABS(SP)-0.1*SS) 94,95,95
36500 94 DMULT = 0.8
36600 95 PJ = DMULT/SS
36700 PA = DMULT/(DMULT*SP+(1.-DMULT)*SS)
36800 K = 0
36900 DO 96 I=1,N
37000 SP = PJ*W(NW+I)
37100 SS = PJ*W(MW+I)
37200 DO 97 J=1,N
37300 K = K+1
37400 W(K) = W(K)+SP*X(J)
37500 AJINV(I,J) = AJINV(I,J)+SS*F(J)
37600 97 CONTINUE
37700 96 CONTINUE
37800 GOTO 38
37900 END

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00100
00200 C THERMODYNAMIC ANALYSIS OF COPPER SEGREGATION USING FREE
00300 C ENERGY MINIMISATION TECHNIQUE
00400 DIMENSION FORT(100),DELG(100),
00500 1PERC(100),AA(100,10),DELT(100),YG(90),X(100)
00600 1,ALPHA(100),XLAM(100),FSUM(100),YSUM(100),PARP(100)
00650 1,Y(100),AB(10),R(10,10),PI(21),BB(10)
00660 1,F(100),YC(10),C(100)
00670 1,BSUM(13,1),COEF(13,13),FB(13)
00700 CHARACTER *6 SYM(100)
00800 CHARACTER *6 SYMB(100)
00900 C NG=NUMBER OF GASEOUS SPECIES
01000 C NC=NUMBER OF CONDENSED SPECIES
01100 C NO=TOTAL NUMBER OF CHEMICAL SPECIES CONCEIVABLE
01200 C MM=NUMBER OF ELEMENTS
01300 DATA NG,NC,MM,IDEBUG/15,6,6,0/
01400 DATA (Y(I),I=1,7)/0.00052,.00596,.0001,.005,.0003,.0001,.0001/
01500 DATA (Y(I),I=8,11)/.0327,.0075,0.0075,.005197
01600 DATA (Y(I),I=12,15)/4*1E-9/
01700 DATA (Y(I),I=16,18)/0.1106,.1316,.733/
01750 DATA (Y(I),I=1,19)/3*.1E-5/
01800 DATA (Y(I),I=1,7)/.7E-7,.8E-7,.2E-12,0.01439,.47E-5,.47E-5,.4E-
01900 1,0.05265/
02000 DATA (Y(I),I=8,11)/0.0155,0.011961,0.0024398,0.0063877/
02100 DATA (Y(I),I=12,15)/.3E-22,.1E-12,.2E-21,.4E-10/
02200 DATA (Y(I),I=16,18)/.128999,.096283,.728671/
02300 C
02400 WRITE (11,3)
02500 3 FORMAT(1H1,/,1X,30X,'THERMODYNAMIC ANALYSIS OF CU-FE-C-H-CL-O
02600 & SYSTEM',29X,50(' '),/,1X,FREE ENERGY AND ATOM COEFFICIENTS='')
02700
02800 NO=22
02900 NN=NC+NG
03000 AP=1.
03100 AR=1.987
03200 CRIT=1.0E-5
03300 AT=298.15
03400 T=1100.
03500 DO 31 I=1,NO
03600 READ (5,8) DELG(I),SYMB(I)
03700 READ (5,2) (AA(I,J),J=1,MM)
03800 31 WRITE (11,602) I,SYMB(I),DELG(I)
03900 &(AA(I,J),J=1,MM)
04000 WRITE (11,6) NG,NC,MM
04100 CPO=0.0645
04200 FO=0.73587
04300 CBN=0.16444
04400 HYC=1.-CPO-CBN
04500 BB(1)=2.*CPO
04600 BB(2)=2.*FO
04700 BB(3)=CBN
04800 BB(4)=HYC
04900 BB(5)=HYC
05000 BB(6)=CPO+3.*FO
05100 WRITE (11,5)
05200 5 FORMAT(/,1X,'START MOLE FRACTIONS OF CU2O,FE2O3,C,HCL(G)='')
05300 WRITE(11,604) CPO,FO,CBN,HYC
05400 WRITE (11,7)
05500 7 FORMAT(/,1X,'ELEMENTAL ABUNDANCE OF CU,C,FE,H,CL,O(SEQUEN)='')
05600
05700 605 WRITE(11,604) (BB(J),J=1,MM)

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05800      DO 60 J=1,MM
05900      AB(J)=0.0
06000      DO 610 I=1,NN
06100      AB(J)=AB(J)+AA(I,J)*Y(I)
06200      WRITE (11,14)
06300      610  FORMAT(/,1X,'MASS BALANCE CONSTRAINTS =')
06400      14  WRITE (11,41)
06500      41  FORMAT(/1X,'INITIAL GAS COMPN (SATISFYING MASS BALANCE CONS)=' )
06600      WRITE(11,604) (Y(I),I=1,NN)
06700      611  FORMAT(6E12.5)
06800      8    FORMAT(F10.5,A6)
06900      2    FORMAT(6F5.2)
07000      6    FORMAT(/,16,5X,A6,5X,F10.5,5X,6F8.1)
07100      604  FORMAT(/,1X,8E15.4)
07200      1032  FORMAT(1X,12E10.2)
07300      DO 1 I=1,NO
07400      FORT(I)=(DELG(I)*1000.)/(AR*T))
07500      1    CONTINUE
07600      WRITE (11,616) T
07700      616  FORMAT(/,45X,,TEMPERATURE =',F10.2)
07800      WRITE (11,75)
07900      75  FORMAT(45X,24('-',))
08000      WRITE (11,21)
08100      21  FORMAT(/1X,'THE (F/RT) VALUES FOLLOW =')
08200      WRITE (11,604) (FORT(I),I=1,NO)
08300      MAXNT=50
08400      MC=NC
08500      MG=NG
08600      XBETA=CRIT
08700      NT=1
08800      DO 33 I=1,MG
08900      SYM(I)=SYMB(I)
09000      33  YG(I)=Y(I)
09100      MN=MG+1
09200      MMN=MN
09300      NNN=NN
09400      IF (MC.EQ. 0) GO TO 300
09500      DO 34 I=MN,NN
09600      SYM(I)=SYMB(I)
09700      34  YC(I)=Y(I)
09800      300  YBAR=0.
09900      DO 50 I=1,MG
10000      YBAR=YBAR+YG(I)
10100      50  C
10200      ... SET UP AND SOLVE MATRIX .....
10300      APRES=DLOG(AP)
10400      DO 10 I=1,MG
10500      C(I)=FORT(I)+APRES
10600      FAC=YG(I)/YBAR
10700      IF (FAC.LT. 1.E-38)FAC=1.E-38
10800      10  F(I)=YG(I)*(C(I)+DLOG(FAC))
10900      IF(MC.EQ. 0) GO TO 13
11000      J=NG
11100      DO 11 I=MN,NN
11200      J=J+1
11300      C(I)=FORT(J)
11400      11  F(I)=Y(I)*C(I)
11500      13  FESUM=0.0
11600      DO 43 I=1,NN
11700      43  FESUM=FESUM+F(I)
11800      IF(NT.NE. 1) GO TO 51

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11900 WRITE (11,61) FESUM
12000 61 FORMAT(/1X,'FREE ENERGY SUM OF MIXTRE =',E18.8)
12100 51 DO 30 J=1,MN
12200 DO 30 K=1,MM
12300 ASUM=0.
12400 DO 20 I=1,MG
12500 SUM=AA(I,J)*AA(I,K)*YG(I)
12600 20 ASUM=ASUM+SUM
12700 30 R(J,K)=ASUM
12800 DO 330 I=1,MG
12900 330 ALPHA(J)=ALPHA(J)+AA(I,J)*YG(I)
13000 KM=MM+MC
13100 NM=MM+MC+1
13200 MMM=MM+1
13300 DO 360 J=MMM,NM
13400 360 ALPHA(J)=0
13500 DO 401 I=1,NM
13600 DO 401 J=1,1
13700 401 COEF(I,J)=ALPHA(I)
13800 MMC=MC+1
13900
14000 IF(MC.EQ.0) GO TO 406
14100 K=MG
14200 DO 402 J=2,MMC
14300 K=K+1
14400 DO 402 I=1,MM
14500
14700 402 COEF(I,J)=AA(K,I)
14800 406 MCC=MMC+1
14900 DO 403 I=1,MM
15000 DO 403 J=MCC,NM
15100 K=J-MMC
15200 403 COEF(I,J)=R(I,K)
15300 DO 407 I=MMM,NM
15400 DO 407 J=2,MMC
15500 407 COEF(I,J)=0.
15600 IF (MC. EQ. 0) GO TO 408
15700 L=NG
15800 DO 404 I=MMM,KM
15900 K=0
16000 L=L+1
16100 DO 404 J=MCC,NM
16200 K=K+1
16300 404 COEF(I,J)=AA(L,K)
16400 408 DO 405 I=NM,NM
16500 K=0
16600 DO 405 J=MCC,NM
16700 K=K+1
16800
16900 405 COEF(I,J)=ALPHA(K)
17000 DO 361 K=1,1
17100 DO 361 J=1,MN
17200 BSUM(J,K)=0.
17300 DO 362 I=1,MG
17400 362 BSUM(J,K)=BSUM(J,K)+AA(I,J)*F(I)
17500 361 BSUM(J,K)=BSUM(J,K)+BB(J)
17600 IF(MC.EQ.0) GO TO 409
17700 DO 363 K=1,1
17800 L=MG
17900 DO 363 J=MMM,KM
18000 L=L+1

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18100 363 BSUM(J,K)=C(L)
18200
18300 409 CONTINUE
18400 DO 364 K=1,1
18500 DO 364 J=NM,NM
18600 BSUM(J,K)=0.0
18700 DO 364 I=1,MG
18800 364 BSUM(J,K)=BSUM(J,K)+F(I)
18900 DO 333 J=1,NM
19000 K=1
19100 FB(J)=BSUM(J,K)
19200 333 CONTINUE
19300 CALL SIMEQ(COEF,FB,NM,KERR,NM)
19400 DO 334 J=1,MN
19500 K=1
19600 334 BSUM(J,K)=FB(J)
19700 XYBAR=BSUM(1,1)
19800 IF(MC.EQ.0) GO TO 103
19900 C NEW X'S FOR CONDENSED SPECIES
20000 J=MG
20100 DO 101 I=2,MMC
20200 J=J+1
20300
20400 101 X(J)=BSUM(1,1)
20500 C NEW X'S FOR GASEOUS SPECIES
20600 103 J=0
20700 DO 102 I=MCC,NM
20800 J=J+1
20900 102 PI(J)=BSUM(I,1)
21000 DO 60 I=1,MG
21100 60 FSUM(I)=-F(I)+YG(I)*XYBAR
21200 DO 110 I=1,NG
21300 PSUM=0
21400 DO 120 J=1,MN
21500 120 PSUM=PSUM+PI(J)*AA(I,J)
21600 YSUM(I)=PSUM*YG(I)
21700 110 X(I)=FSUM(I)+YSUM(I)
21800 C LAMBDA AND DIRECTIONAL DERIVATIVE
21900 XLAMBD=1.
22000 310 DO 86 I=1,NN
22100 DELT(I)=X(I)-Y(I)
22200 IF(DELT(I).GE.0.) GO TO 86
22300 XLAM(I)=Y(I)/(-DELT(I))
22400 XLAMBD=DMIN1(XLAMBD,XLAM(I))
22500 86 CONTINUE
22600 DEBAR=0.
22700 DO 87 I=1,MG
22800
22900 87 DEBAR=DEBAR+DELT(I)
23000 93 DFDL=0.0
23100 DO 88 I=1,MG
23200 96 FAC=(YG(I)+XLAMBD*DELT(I))/(YBAR+XLAMBD*DEBAR)
23300 IF(FAC.GT.0) GO TO 82
23400 XLAMBD=0.05*XLAMBD
23500 GO TO 96
23600 82 DFDL=DFDL+DELT(I)*(C(I)+DLOG((YG(I)+XLAMBD*DELT(I))/(YBAR+XLAMB
23700 1*DEBAR)))
23800
23900 88 CONTINUE
24000 IF(MC.EQ.0) GO TO 84
24100 DO 83 I=MN,NN

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24200      83      DFDL=DFDL+C(I)*DELT(I)
24300      84      IF(DFDL.LT.0) GO TO 89
24400          IF(XLAMBD.GT.1.E-38) GO TO 91
24500          KX=KX+1
24600          GO TO 191
24700      91      XLAMBD=0.5*XLAMBD
24800          GO TO 93
24900      89      IF(IDEBUG.NE.0) WRITE (11,1021)XLAMBD
25000      1021    FORMAT(/,1X,7H,LAMBDA=E15.5/)
25100      191      IF (XLAMBD. EQ. 0) GO TO 2001
25200
25300      C      NEW Y'S FOR GASEOUS & CONDENSED SPECIES
25400          DO 76 I=1,NN
25500          Y(I)=Y(I)+XLAMBD*DELT(I)
25600      76      CONTINUE
25700          DO 77 I=1,MG
25800      77      YG(I)=Y(I)
25900          IF (MC.EQ. 0) GO TO 351
26000          J=NG
26100          DO 74 I=MN,NN
26200          J=J+1
26300
26400      74      YC(J)=Y(I)
26500      351      BETA=0.
26600          DO 85 I=1,NN
26700      85      BETA=BETA+DABS(DELT(I))
26800          IF (BETA. LT. XBETA) GO TO 140
26900          IF (NT. GE. MAXNT) GO TO 600
27000          NT=NT+1
27100          GO TO 300
27200
27300      600      XBETA=XBETA+CRIT
27400          MAXNT=MAXNT+50
27500          NT=NT+1
27600          GO TO 300
27700      140      PSUM=0.
27800          DO 131 I=1,MG
27900
28000      131      PSUM=PSUM+Y(I)
28100          DO 132 I=1,MG
28200      132      PARP(I)=(Y(I)/PSUM)
28300      78      SUMY=0.0
28400          DO 370 I=1,NN
28500      370      SUMY=SUMY+Y(I)
28600          DO 340 I=1,NN
28700      340      PERC(I)=(Y(I)/SUMY)
28800          IF (MC. EQ. 0) GO TO 2000
28900          J=NG
29000          DO 350 I=MN,NN
29100          J=J+1
29200      350      PERC(J)=PERC(I)
29300      2000      WRITE (11,16) NT
29400      16      FORMAT(/1X,28HNO. OF ITERATIONS REQUIRED =I5/)
29500          WRITE (11,201) XBETA
29600      201      FORMAT(/1X,5HBETA=E12.4/)
29700          WRITE (11,22)
29800      22      FORMAT(/1X,'FINAL EOBM COMPN. OF CHEMICAL SPECIES =')
29900          WRITE (11,32)
30000      32
30100      32      FORMAT(/6X,1HI,21X,4HY(I)/)
30200          DO 44 I=1,NN

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30300      19      FORMAT(1X,I6,3X,A6,3E20.8,/)
30400      44      WRITE (11,19) I,SYMB(I),Y(I),PERC(I),PARP(I)
30500      WRITE (11,61) FESUM
30600      DO 615 J=1,MM
30700      AB(J)=0.0
30800      DO 615 I=1,NN
30900      615      AB(J)=AB(J)+AA(I,J)*Y(I)
31000      WRITE(11,23)
31100      23      FORMAT(/,1X,'MASS CONSTRAINTS CHECK (WHETHER SATISFIED ?)=')
31200      WRITE (11,604) (AB(J),J=1,MM)
31300      WRITE (11,24)
31400      24      FORMAT(/1X,'LAMBDA VALUES FOLLOW=')
31500      WRITE (11,604) (PI(J),J=1,MM)
31600      J=15
31700      FORT1=0.
31800      DO 4 I=1,MM
31900      4      FORT1=FORT1+(PI(I)*AA(J,I))
32000      FORT1=FORT1(15)-FORT1
32100      PRINT ,FORT1
32200      IF (FORT1.GT. 0) GO TO 2001
32300      WRITE (11,15)
32400      15      FORMAT(/,'CU20 IS PRESENT IN THE MIXTURE ')
32500      2001     CONTINUE
32600      WRITE (11,25)
32700      25      FORMAT(1H1)
32800      STOP
32900      END
33000      SUBROUTINE SIMEQ(A,B,N,KERR,IDIM)
33100
33200      C      THIS SUBROUTINE SOLVES A SYSTEM
33300      C      OF LINEAR EQUATIONS
33400      C      BY METHOD OF PIVOTAL CONDENSATION
33500      C      A:NXN MATRIX
33600      C      B:ARRAY CONTAINING N CONSTANTS
33700      C      N:ORDER OF THE SYSTEM
33800      C      KERR:INDIICATOR OF SUBROUTINE
33900      C      ONE IF SYSTEM SINGULAR
34000      C      ZERO OTHERWISE
34100      C      READ A COLUMN BY COLUMN
34200      DIMENSION A(IDIM,IDIM),B(IDIM)
34300      DIMENSION L(50),M(50)
34400      EPS=1E-6
34500      EPSOR=EPS*EPS
34600      KERR=0
34700      C      CLEAR OUT PERMUTATION VECTORS
34800      DO 3 I=1,N
34900      M(I)=0
35000      3      L(I)=0
35100      C      LOOP FOR N PIVOT POINTS
35200      DO 14 KP=1,N
35300      P=0.
35400      PSQR=0.
35500      DO 7 I=1,N
35600      DO 7 J=1,N
35700      IF (M(I))7,4,7
35800      4      IF (L(J))7,5,7
35900      5      T=A(I,J)
36000      TSQR=T*T
36100      IF (TSQR-PSQR)7,7,6
36200      6      P=T
36300      PSQR=TSQR

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36400      KR=I
36500      KC=J
36600      7      CONTINUE
36700      IF (PSQR-EPSQR)17,17,8
36800
36900      8      M(KR)=KC
37000      L(KC)=1
37100      C      DIVIDE KEY ROW BY PIVOT
37200      DO 10 J=1,N
37300      IF (L(J))10,9,10
37400      9      A(KR,J)=A(KR,J)/P
37500      10     CONTINUE
37600      BKR=B(KR)/P
37700      B(KR)=BKR
37800      C      SUBTRACT MULTIPLE OF KEY ROW FROM
37900      C      OTHER ROWS
38000      DO 14 I=1,N
38100      IF (I-KR)11,14,11
38200      11     R=A(I,KC)
38300      DO 13 J=1,N
38400      IF (L(J))13,12,13
38500      12     A(I,J)=A(I,J)-R*A(KR,J)
38600      13     CONTINUE
38700      B(I)=B(I)-R*BKR
38800      14     CONTINUE
38900      C      REORDER RESULTS
39000      DO 15 I=1,N
39100      IP=M(I)
39200      15     A(IP,1)=B(I)
39300      DO 16 I=1,N
39400      16     B(I)=A(I,1)
39500      RETURN
39600      C      ERROR ACTION
39700      17     KERR=1
39800      RETURN
39900      END

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